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A STUDY OF LEACHATE FROM DREDGED MATERIAL IN UPLAND AREAS AND/O--ETC.(U)

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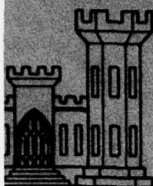
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DREDGED MATERIAL RESEARCH PROGRAM



TECHNICAL REPORT D-78-20

A STUDY OF LEACHATE FROM DREDGED MATERIAL IN UPLAND AREAS AND/OR IN PRODUCTIVE USES

by

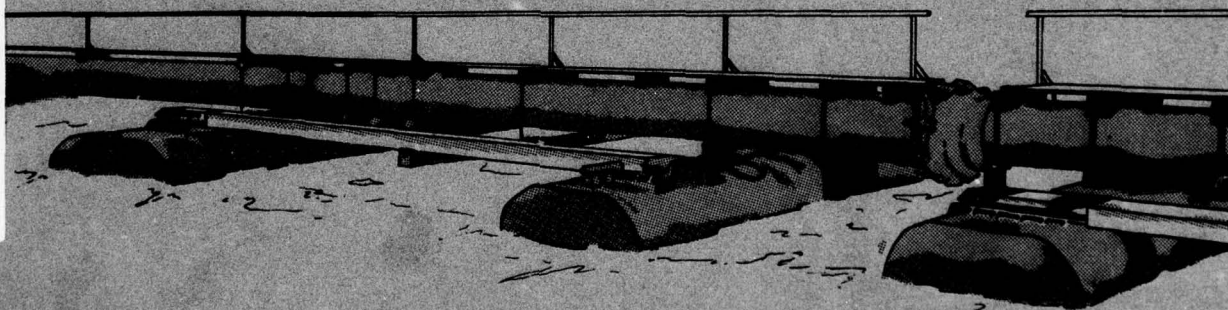
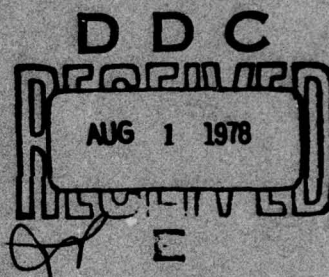
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June 1978

Final Report

Approved For Public Release; Distribution Unlimited



Prepared for Office, Chief of Engineers, U. S. Army
Washington, D. C. 20314

Under Contract No. DACW39-76-C-0069
(DMRP Work Unit No. 2D02)

Monitored by Environmental Laboratory
U. S. Army Engineer Waterways Experiment Station
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IN REPLY REFER TO: WESYV

31 July 1978

SUBJECT: Transmittal of Technical Report D-78-20

TO: All Report Recipients

1. The technical report transmitted herewith represents the results of Work Unit 2D02 of Task 2D, Confined Disposal Area Effluent and Leachate Control, of the Corps of Engineers' Dredged Material Research Program (DMRP). Task 2D was a part of the Environmental Impacts and Criteria Development Project, which in part was concerned with establishing a data base and developing mitigative measures for different modes of dredged material disposal. The work units in Task 2D deal more specifically with the environmental impact of effluents and leachates produced from the confined land disposal of dredged material.

2. Work Unit 2D02 involved the generation of leachate from 16 large plexiglas lysimeters under different environmental conditions. The major objectives of the study were: (a) to assess the potential adverse impacts on groundwater of leachates generated from dredged material in land containment areas; (b) to determine which major environmental variables (e.g., pH and oxidation-reduction conditions), or combinations of the major measurable variables, might have synergistic or attenuative influence on the mobility of various contaminants; (c) to assess how dredged material leachates are modified upon passage through oxidized surface soils lying beneath a disposal area; and (d) to determine what influence recently emplaced dredged material might have on the physico-chemical conditions in the underlying soil profile, and how the resultant changes might affect contaminant mobility in the leachates and also the generation of mobile contaminants from the soil. The study more specifically looked at the influence of different types and levels of organic matter on the mobility of contaminants (especially trace metals) by: (a) using dredged material from five different locations (environments) with each having a different organic content; (b) choosing two interacting soils that contained both qualitative and quantitative differences in organic matter content; (c) leaching certain lysimeter columns with a landfill leachate that contained a high level of soluble organic carbon; and (d) leaching certain columns with a characterized fulvic acid solution, which should represent worst-case conditions at a solid waste disposal site or conditions in a soil of high organic content (e.g., marshland disposal). The influences of alkaline groundwater conditions and acidic rainfall on contaminant mobility were also assessed.

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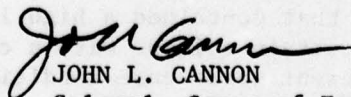
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3. The results from this study show that no single mechanism can account for the migratory trends of all contaminants in dredged material or subsurface soil leachates. In the dredged material pore water, values for pH, Eh (oxidation), total organic carbon, alkalinity, and manganese generally showed a slight increase over time; the other parameters either remained relatively stable (total phosphorus, orthophosphate phosphorus, and magnesium), showed decline (total Kjeldahl nitrogen, ammonium-N, copper, calcium, sodium, and potassium), or showed highly variable trends (cadmium and zinc). Synthetic chlorinated hydrocarbons (e.g., PCBs and DDT analogs) were generally at undetectable levels. After the dredged material leachates migrated through subsurface soil profiles, there were several major changes in leachate quality. The solution pH was regulated by the pH and nature of the specific type of soil. A forest soil containing an above-average organic content tended to increase total organic carbon and decrease alkalinity and pH. Both soils used in the study acted as a generating source for soluble iron, manganese, calcium, potassium, nitrate nitrogen, and total Kjeldahl nitrogen. In general, soluble cadmium, copper, and lead were removed by the soils; sodium and ammonia nitrogen were initially attenuated, but this trend became less prevalent with long-term leaching. The migration of soluble salts (e.g., sodium and chloride ions) could be a problem in certain disposal areas containing saline dredged material. The migration of soluble ($<0.45\text{-}\mu$ filterable) phosphorus and mercury was not found to be a problem, although particulate mercury and total phosphorus were occasionally released at moderate levels. The migration of chlorinated hydrocarbons from the soils was negligible.

4. Although dilution effects alone should rapidly ameliorate any groundwater contamination problems, this study indicated that levels of ammonia and nitrate nitrogen, alkalinity, iron, manganese, total lead, and possibly zinc in the leachates from the dredged material samples used in the columns could exceed present water-quality criteria. However, many excessive concentrations (e.g., for manganese and iron) were derived from the soil as a result of changes induced by emplacement of overlying dredged material.

5. The data in this publication should be used, in context with field leachate findings, for determining the impact of land disposal on groundwater quality. It is anticipated that the results and discussion contained herein will aid those persons concerned with criteria development, water-quality monitoring, environmental impact reports, permit programs, or other regulatory functions.



JOHN L. CANNON
Colonel, Corps of Engineers
Commander and Director

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| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|--|---|
| 1. REPORT NUMBER Technical Report D-78-20 | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle) A STUDY OF LEACHATE FROM DREDGED MATERIAL IN UPLAND AREAS AND/OR IN PRODUCTIVE USES | 5. TYPE OF REPORT & PERIOD COVERED Final report | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s) James L. Mang, Ronald J. Lofy James C. S. Lu, Robert P. Stearns | 8. CONTRACT OR GRANT NUMBER(s) Contract No. DACW39-76-C-0069 | |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS SCS Engineers 4014 Long Beach Boulevard Long Beach, California 90807 | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS DMRP Work Unit No. 2002 | |
| 11. CONTROLLING OFFICE NAME AND ADDRESS Office, Chief of Engineers, U. S. Army Washington, D. C. 20314 | 12. REPORT DATE June 1978 | |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) U. S. Army Engineer Waterways Experiment Station Environmental Laboratory P. O. Box 631, Vicksburg, Miss. 39180 | 13. NUMBER OF PAGES 435 | |
| | 15. SECURITY CLASS. (of this report) Unclassified | |
| | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE | |
| 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. | | |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) | | |
| 18. SUPPLEMENTARY NOTES | | |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Containment areas Leaching (Soils) Dredged material Lysimeters Leachates Waste disposal sites | | |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A laboratory lysimeter study was conducted to determine the composition of subsurface leachates generated from each of five different dredged materials, each combined with one of two different subsurface soil profiles. Sixteen 30-cm-diam Plexiglas lysimeter columns were consecutively filled with equal depths of homogeneous, oxidized native soil and anoxic dredged material (total profile of 60 cm). The dredged materials were obtained from land disposal areas located near Mobile, Ala. (saline silty clay), Sayreville, N. J. (saline silty loam), Grand Haven, Mich. (freshwater sandy clay loam), Seattle, Wash. (saline silty loam), and Houston, Tex. (saline silty clay). The native soils included a low organic, moderately permeable semiarid soil (Perkins loam) obtained from arable land near Hemet, Cal., and a highly organic upland sandy loam soil, obtained from a temperate coniferous forest near Lake Arrowhead, Cal. (Continued) | | |

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20. ABSTRACT (Continued).

The primary leaching solution was distilled water (rainwater leach), which was added in pulses to simulate alternate wet-dry cycling prevalent in most land containment areas. Other leaching fluids consisted of distilled water acidified to pH 4.5 with sulfur dioxide (acid rainfall leach), hard water buffered with bicarbonate (alkaline groundwater simulation), and leaching fluids containing high organic contents (a leachate obtained from a solid waste landfill site and a characterized fulvic acid solution, to represent conditions at a solid waste disposal site or in a marsh or swamp environment). Leaching tests were performed for periods of 3, 6, and 9 months for different columns. Parameters analyzed included major elements, trace metals, PCB's, chlorinated pesticides, nutrients (nitrogen and phosphorus compounds, organic carbon), chloride, sulfides, and various gross physicochemical parameters (alkalinity, Eh, pH, conductivity).

The results from this study indicate that leachate quality may be governed by both the dredged material and underlying soil. The leachates (interstitial water) from the dredged material tended to show slight time-dependent increases in pH, Eh, total organic carbon, alkalinity, and manganese. Concentrations of soluble total phosphorus, orthophosphate phosphorus, and magnesium remained relatively stable, while soluble organic and ammonium nitrogen, copper, calcium, sodium, and potassium showed continual decreases in concentration. Cadmium and zinc trends were highly variable during the course of the leaching tests. Chlorinated hydrocarbons (PCB's and chlorinated pesticides) were generally at undetectable levels.

The soils tended to regulate the leachate pH, organic carbon, and alkalinity, and they served as a source for soluble iron, manganese, calcium, potassium, nitrate nitrogen, and total Kjeldahl (organic plus ammonium) nitrogen. Soluble cadmium, copper, and lead were generally removed by the soils. Long-term leaching tended to increase ammonium nitrogen levels in final leachates. The attenuative capacity of the soils for soluble sodium, potassium, and calcium decreased during the six-month tests, especially for columns containing saline dredged material. This suggests a potential problem for salt migration, especially through moderately permeable dredged material and subsurface soils. The migration of soluble (>0.45- μ filterable) phosphorus and mercury was not observed to create a problem for leachates, although particulate mercury and phosphorus were occasionally released at moderate levels. The chlorinated pesticide and PCB levels in final leachates were usually nil.

Since drying of the dredged material failed to occur during the wet-dry cycling studies, many of the observed fluctuations in leachate quality were probably regulated by changes in the flow rate, induced by variations in the hydraulic head. The short-term application of acid rainwater and alkaline groundwater leaches had negligible impact on leachate quality; the acid leach slightly decreased the capacity of the system for removing alkalinity and calcium, probably by dissolving calcite from near the surface of the sediment profile. The municipal-waste leaching fluid also failed to cause major impact on leachate quality, although a slight increase in total organic carbon was observed; this was probably promoted by the poor attenuative capacity of the soils for this parameter combined with a high organic carbon level in this leaching solution.

The controlling mechanisms affecting the migration of different constituents in dredged material/interfacing soil systems were found to be very complex. Solubilization could control the levels of calcium, magnesium, pH, alkalinity, phosphorus, and all trace metals in the dredged material. Calcite solubilization specifically regulated the levels of calcium and alkalinity and strongly controlled pH. For many trace metals, the increased oxidation observed in the dredged material probably regulated soluble levels through dissolution of sulfide complexes and precipitation of carbonate, hydroxide, and/or oxyhydroxide solids. The solubility differences for these new solids, which are different for each constituent, probably regulated soluble levels. However, complexation with mobile inorganic and organic compounds can greatly change the expected soluble concentrations. Adsorption, ion exchange, and dilution seemed to play dominant roles for many highly mobile species (sodium, potassium, calcium, chloride, and ammonium nitrogen) as well as for most trace metals.

In the soil system, adsorption of constituents onto solids seemed to be an important mechanism for attenuation, especially for ammonia nitrogen, cadmium, copper, mercury, and lead. Precipitation reactions in the soil could attenuate phosphorus and some trace metals as well as control pH and alkalinity levels. The mobility of constituents generally seemed to be governed by the inherent properties of the soils (especially by pH and Eh changes) and not by the nature of the leaching solutions.

Groundwater dilution effects were not incorporated into this study, and the interacting soils were emplaced in a disturbed and oxidized state. Thus, the results probably represent worst-case conditions for contaminant mobility. However, the levels of ammonia and nitrate nitrogen, alkalinity, iron, manganese, zinc, and total (particulate) lead were occasionally in excess of present criteria. The data thus strongly suggest that the groundwater and soil conditions should be carefully considered when choosing a prospective land disposal site.

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SUMMARY

The disposal of dredged material in upland areas (removed from tidal influence) may be an attractive alternative to other disposal options, or in some cases, a necessity because of local environmental conditions. Due to the physical and chemical characteristics of dredged material, concern has risen as to the impact of leachates from such disposal areas on local water resources. The purpose of this project was to evaluate the potential effects of leachates from upland dredged material disposal areas on groundwater quality.

A laboratory simulation was developed using Plexiglas lysimeter columns filled with two types of interfacing soils and dredged materials obtained from five actual upland disposal sites. Various leaching solutions were passed through both a dredged material and an interfacing soil placed in tandem in a Plexiglas lysimeter. The experimental set-up may be seen on Figure 3.

Several types of water samples were studied. Interstitial water samples (those water samples withdrawn from the dredged material) and final leachate samples were obtained after leaching fluids, introduced at the top of the lysimeter columns, had an opportunity to pass through both the dredged material and the interfacing soil. In addition, in "soil blank" columns water samples were obtained after the leaching fluids had an opportunity to contact only the interfacing soil. Tables 11 and 12 delineate the combinations of dredged material and interfacing soils utilized in the experimentation. Various analytical tests were performed on the water samples as well as on the dredged material and interfacing soil samples. The tests performed on the water

samples are listed on Table 14; parameters analyzed for in dredged material and interfacing soils on Table 13.

The study showed that the migration of constituents in dredged material/interfacing soil systems is complex; no single mechanism can account for the various trends and levels of migration. The major mechanisms that appeared to affect the migration of constituents from dredged material were solubilization, adsorption, complexation, redox reactions, ion exchange, and dilution.

The attenuation of soluble constituents when fluids moved through interfacing soils was usually governed by adsorption, precipitation, and ion exchange. However, the elution of soluble constituents was usually regulated by dissolution, complexation, desorption, hydrolytic action, ion exchange, and bioconversion reactions. Physical scouring was the primary controlling mechanism for the release of constituent particulate forms from soil. Moreover, it was also found that chlorinated hydrocarbons did not mobilize from dredged material to any great extent.

The potential impact of dredged material leachate on water quality appears to be a function of the chemical composition and physical characteristics of the dredged material and interfacing soils, as well as the designated use of the receiving water body. Based on the experimental results, pH, orthophosphate, cadmium, copper, mercury, and soluble lead in dredged material leachates are not expected to present water quality problems. However, the levels of ammonia-nitrogen, nitrate-nitrogen, alkalinity, iron, manganese, total lead, and possibly zinc observed in such leachates exceed selected water quality criteria and, in the absence of any dilution effects, could pose water quality problems.

Using experimental results, three indices were developed to provide a qualitative measure of potential for groundwater contamination by various constituents in dredged material leachates. The indices were as follows:

- Mobility Index (MI) - the ratio of the soluble concentration of various constituents in leachate to that in the interstitial water prior to passage through the interfacing soils.
- Evaluatory Index (EI) - the ratio of the soluble concentration of a constituent in the leachate to the EPA drinking water standard for that constituent.
- Impact Index (II) - the product of the Mobility Index and the Evaluatory Index of a particular constituent.

The Mobility Index measures the attenuative capacity of the interfacing soil for a constituent contained in the dredged material leachate. A Mobility Index value of 1 means a constituent passes through the soil virtually unchanged in concentration. A Mobility Index value <1 indicates that the constituent is being attenuated by the soil, whereas, if the index value is >1 , the constituent is being released by the soil itself. Average MI values in the two soils and for the various leachate constituents measured during this experiment are shown in Table 94. As can be seen, manganese, nitrate-nitrogen, total phosphorus, and iron were strongly released from the soils ($MI > 10$). Calcium, orthophosphate, TOC, zinc, chloride, total Kjeldahl nitrogen, potassium, mercury, and magnesium were moderately released ($1 < MI < 10$). Copper, sodium, ammonia-nitrogen, lead, and cadmium were attenuated ($MI < 1$) by the soils used in this experiment.

The Evaluatory Index (EI) provides a "worst case" measure of the potential impact of a leachate constituent on groundwater; EI values for the various constituents for the two types of soils studied are presented in Table 93. The EI values of the constituents below lead on the

tabulation were found to be <1 ; these constituents will probably not cause problems when leachates discharge into a receiving water body used for a public water supply.

The Impact Index (the Mobility Index times the Evaluatory Index) is a means of evaluating the potential impact of dredged material leachates on the environment. The Impact Index values, shown on Table 94, list the constituents in descending order, providing a relative ranking of the expected impact of each constituent on ground or surface waters. It focuses attention on the constituents with the highest contamination potential: manganese, TOC, iron, and total phosphorus. Total Kjeldahl nitrogen, nitrate-nitrogen, chloride, calcium, and sodium may cause environmental problems, but impacts of magnesium, potassium, orthophosphate, ammonia-nitrogen, mercury, lead, zinc, cadmium, and copper would be negligible, based on the simulated dredged material/interfacing soil-leaching fluid systems evaluated in this experiment.

Leachate problems at upland dredged material disposal sites can be mitigated by installing artificial liners or underdrain collection systems. Factors dictating use of one specific method over another are site-specific and must be considered on a site-by-site basis. When dredged material leachates are collected, treatment may consist of recirculation, biological and/or physical/chemical treatment. Although no bench scale tests were performed, it appears that physical/chemical treatment holds the most promise in this area.

PREFACE

This report presents the results of an intensive field and laboratory investigation of leachates from dredged material in upland areas under Contract Number DACW39-76-C-0069, between the U.S. Army Engineer Waterways Experiment Station (WES) and SCS Engineers (SCS).

James L. Mang served as Project Manager for the SCS research effort, with technical assistance from Drs. Ronald J. Lofy and James C. S. Lu. Robert P. Stearns served as Project Director for SCS. Dr. Kenneth Y. Chen of the University of Southern California Department of Environmental Engineering served as project advisor and technical reviewer.

Special thanks are due Jacqueline Ivy, technical editor, Dr. Hang Tan Phung, research scientist, Kenneth Borgers and Mark Bulot, research technicians, and Susan Brown and Lona Taylor, typists.

This contract was managed by Ronald E. Hoeppel, Environmental Impacts and Criteria Development Project (EICDP), Environmental Laboratory (EL), WES, under the supervision of Dr. Robert M. Engler, Manager, EICDP. The study was under the general supervision of Dr. John Harrison, Chief, EL.

Director of WES during preparation of this report was COL J. L. Cannon, CE. Technical Director was Mr. F. R. Brown.

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GLOSSARY

- acid rainfall: Depression of pH levels in rainfall primarily due to increasing amounts of sulfuric and nitric acids in the atmosphere derived from sulfur dioxide and nitrogen oxides emitted into the atmosphere by combustion processes.
- acclimation: Adaption of a species or population over several generations to a changed environment.
- activity coefficient: The ratio of the activity of a constituent to its concentration.
- adsorption: (1) The adherence of a gas, liquid, or dissolved material on the surface of a solid, (2) A change in concentration of gas or solute at the interface of a two-phase system.
- ammonification: Bacterial decomposition of organic nitrogen to ammonia.
- anoxic: Oxygen deficient.
- assimilation: The absorption and utilization of a nutrient by an organism.
- attenuation: The decrease in concentration of a particular constituent in solution when passing through a leaching medium for some fixed time or distance.
- biochemical oxygen demand (BOD): The amount of oxygen required for the biological oxidation of the organic matter in a liquid.
- bioconversion: Biological conversion of a substance from one form to another.
- biological degradation: The destruction or mineralization of either natural or synthetic organic materials by the microorganisms populating soils, natural bodies of water or wastewater treatment systems.
- cation-exchange capacity (CEC): The sum total of exchangeable cations that a soil can adsorb.
- centrifugation: Separation of a liquid into soluble and solid fractions by utilization of a centrifuge.

GLOSSARY (Continued)

chelation: The formation of an inner complex compound, soluble in water, in which the same molecule is attached to a central atom at two different points forming a ring structure.

complexation: Any combination of cations with molecules or anions containing free pairs of electrons (bases).

coprecipitation: Simultaneous precipitation of more than one substance.

crystalline lattice: A lattice from which the structure of a crystal may be obtained by associating with every lattice point an assembly of atoms identical in composition, arrangement, and orientation.

decomplexation: The disassociation of either cations with molecules or anions containing free pairs of electrons.

denitrification: A biological process in which gaseous nitrogen is produced from nitrite and nitrate.

deposition: The act or process of settling solid material from a solution.

diffusion: The spontaneous movement and scattering of constituents in a liquid, solid, or gas.

dissolution: Dissolving of a material.

elution: The increase in concentration of a particular constituent in solution when passing through a leaching medium for some fixed time or distance.

exchangeable ions: Ionic species on or in a solid medium which can be replaced by another soluble ion(s) through ion exchange.

Freundlich isotherm equation: An adsorption equation which states the relationship between the bulk activity temperature, equilibrium constant, and adsorption capacity.

groundwater intrusion: Movement of a water mass into a particular groundwater aquifer.

GLOSSARY (Continued)

hydrolysis: The reaction of a solute with water in aqueous solution.

hydrolytic reaction: The reaction of an organic (or inorganic) compound in water, i.e., water effects a double decomposition with another compound, hydrogen going to one compound and hydroxyl to the other.

interstitial water: Water contained in the pore space of solid material such as soil, dredged material, or rocks.

ion activity coefficient: The ratio between the activity and total concentration of a component in an aqueous solution or gas mixture.

ion exchange: A chemical reaction in which mobile ions of a solid are exchanged (equivalent for equivalent) for ions of like charge in solution.

isomorphous replacement: The replacement of one atom by another of similar size in a crystal lattice without disrupting or changing the crystal structure of the mineral.

isotherm: A relationship between two variables in which temperature is held constant.

Langmuir isotherm equation: An adsorption equation that describes the relationship between bulk activity, temperature, equilibrium constant, and adsorption capacity.

leachate: A solution resulting from the separation or dissolving of soluble or particulate constituents from solid leaching media by percolation of water.

ligand: The molecule, ion, or group bound to the central atom in a chelate or a coordination compound.

mass action law: The law that states that the rate of a chemical reaction for a uniform system at constant temperature is proportional to the concentrations of the substances reacting.

microbial degradation: See biological degradation.

GLOSSARY (Continued)

migration: Movement of constituents in liquids, solids or gases.

mineralization: The process by which elements combined in organic form are converted into inorganic forms.

mobility: Freedom of constituents to move, either in random motion or under the influence of fields or forces.

nitrification: The conversion of nitrogenous matter into nitrates by bacteria.

nitrogen fixation: The utilization of free nitrogen in the formation of plant tissue in leguminous plants, bacterial protoplasm, or algal protoplasm by appropriate biological activity.

nonpolar: Pertaining to an element or compound which has no permanent electric dipole moment.

nucleation: The formation of new crystal nuclei in super-saturated solutions.

nutrient: Any substance (such as nitrogen and phosphorus compounds) assimilated by organisms which promotes growth and replacement of cellular constituents.

oxidation: The addition of oxygen to a compound or the loss of electrons from a substance.

oxidizing environment: An environment with low electron activity. In this study, oxidizing is defined as the state where oxygen is present and hydrogen sulfide is absent.

permeability: The ease with which gases, liquids, or plant roots penetrate or pass through a bulk mass of solid material such as soil, sediment, or dredged material.

permutation: A function which rearranges a finite number of symbols; a one-to-one function of a finite set onto itself.

pH: The reciprocal of the logarithm of the hydrogen-ion concentration.

GLOSSARY (Continued)

- porosity: The volume percentage of the total bulk not occupied by solid particles.
- precipitate: A substance separating, in solid particles, from a liquid as the result of a chemical or physical change.
- precipitation: The phenomenon that occurs when a substance held in solution in a liquid passes out of solution into solid form.
- receiving waters: A natural watercourse, lake, or ocean into which treated or untreated wastewater is discharged.
- redox potential (Eh): The potential required to transfer electrons from the oxidant to the reductant and used as a qualitative measure of the state of oxidation in systems.
- redox reaction: Oxidation reduction reaction.
- reducing environment: An environment with high electron activity. In this study, reducing is defined as the state where hydrogen sulfide is present.
- reversible chemical reaction: A chemical reaction that can be made to proceed in either direction by suitable variations in the temperature, volume, pressure, or quantities of reactants or products.
- saturation: A condition reached by a material, whether it be in solid, gaseous, or liquid state, that holds another material within itself in a given state in an amount such that no more of such material can be held within it in the same state.
- scouring: A physical erosion process resulting from the action of the flow of air, ice, or water.
- solid solution: A homogeneous crystalline phase composed of several distinct chemical species, occupying the lattice points at random and existing in a range of concentrations.
- solid transformation: The change of geochemical solid phases, i.e., from cadmium sulfide solid to cadmium carbonate solid.

GLOSSARY (Continued)

solubility product constant: A type of simplified equilibrium constant, K_{sp} , defined for and useful for equilibria between solids and their respective ions in solution.

solubilization: A chemical mechanism through which a solid species is converted to a soluble species.

solution flux: The amount of solution (i.e., leaching fluid) flowing across a given area of leaching medium per time unit.

sorption: A general term used to encompass the processes of adsorption, absorption, desorption, ion exchange, ion retardation, chemisorption, and dialysis.

straining effect: The effect of filtering out of particles or particulates by the leaching medium through which a fluid is passing.

thermodynamic equilibrium: Property of a system which is in mechanical, chemical, and thermal balance.

TOC: Total organic carbon content in a particular sample.

trace metals: Metals which exist in the environment in minute quantities.

transport phenomena: Reason for the migration of a constituent in a liquid, solid or gas material.

Van der Waals interparticle attraction: An attractive force between two atoms or nonpolar molecules, which arises because a fluctuating dipole moment in one molecule induces a dipole moment in the other, and the two dipole moments then interact.

volatilization: The conversion of a chemical substance from a liquid or solid state to a gaseous or vapor state by the application of heat, by reducing pressure, or by a combination of these processes.

A STUDY OF LEACHATE FROM DREDGED MATERIAL
IN UPLAND AREAS AND/OR IN PRODUCTIVE USES

PART I: INTRODUCTION

Purpose

1. To maintain navigable waterways, each year the U.S. Army Corps of Engineers dredges approximately 290,520,000 cu m (380,000,000 cu yd) of sedimentary materials from our nation's rivers and harbors. Such dredging is necessary to the economics of the shipping industry: a channel or harbor must be dredged to sufficient depth so vessels can be filled to capacity, or shipping will not be cost-effective. Should harbors and channels not be dredged deep enough, the nation's economy could well be affected.

2. The disposal of this vast amount of dredged material poses a possible ecological problem since a wide variety of water to solid material ratios exist, depending upon the dredging operations, and since the material is disposed on a variety of environments:

- Open water,
- Marshlands,
- Artificially created islands, and
- Upland areas (removed from tidal influence).

The environmental effects of disposal on each of these areas are site specific, many not completely understood.

3. The objective of the U.S. Army Engineer Waterways Experiment Station (WES) Dredged Material Research Program (DMRP) is to investigate and evaluate the environmental effects of dredging and subsequent disposal of dredged material.

4. Two major environmental impacts may occur when dredged material is disposed in upland areas: 1) runoff into surface waters from the dredged slurry itself or from

rainwater that has had an opportunity to contact the site surface yet cannot penetrate the dredged material and underlying soil; and 2) leachate created when rainfall or water associated with dredging operations permeates the dredged material and underlying soils into groundwaters. It is the second impact that this project is designed to investigate.

5. Due to strict water-quality legislation, open-water disposal practices have been somewhat curtailed. Thus, confined land disposal is even more a possibility. At present, however, there is little information available on the physiochemical transformation, migration, or fate of contaminants associated with the disposal of dredged material into confined land-disposal areas.

6. For example, little is known about the formation of leachates. It is possible that degradation of groundwater may occur when leachates permeate into groundwater underlying upland disposal areas. The extent of this degradation and the environmental conditions under which it will occur have not been documented to any great extent. To understand adverse consequences of upland disposal of dredged material, it is essential that the contaminants in leachates and the environmental conditions for their presence and chemical form be clearly understood.

Approach

7. A laboratory experiment was designed to assess the potential adverse impacts on groundwater of dredged material disposal on upland areas. An assortment of dredged material types was obtained from actual upland disposal sites and placed in Plexiglas lysimeters with various interfacing soils for testing under a variety of simulated conditions. The environmental simulations included:

wet-dry rainfall cycle, groundwater or acid-rainfall intrusion, interaction with municipal leachate, and leaching with a complexing organic acid solution. Various leaching fluids were allowed to permeate through each type of dredged material and its interacting soil. Samples of leachate were withdrawn following passage through the material. In addition, interstitial water samples were obtained from the dredged material.

8. Chemical analyses were performed on both leachate sample types to estimate the concentrations of chemical constituents in leachates resulting from the upland disposal of dredged material.

Scope

9. This project was to investigate and evaluate various aspects of the production, movement, collection, treatment, and disposal of leachates. Special attention was to be given to the methodology required on a laboratory or field scale to evaluate problems associated with leachates.

10. An experimental procedure was to be designed to assess the characteristics of leachate from dredged material in upland areas. The procedure was to allow an assessment of pertinent physical and chemical parameters of dredged material as related to leachate characteristics. Upon completion of the leaching experiments, an assessment of the quality of dredged material leachates was to be made. Preliminary recommendations for treatment, disposal practices, and/or disposal site selection were to be included.

PART II: LITERATURE REVIEW

11. Concepts discussed in this section are presented as background for understanding constituent mobilization and attenuation that may occur in dredged material and soils when dredged material is disposed in upland areas. These concepts will be referred to in the following discussions on experimental data results.

12. Both the dredged material and soils are dynamic, complex, biological, chemical and physical systems. A plethora of controlling mechanisms (redox reaction, diffusion, sorption, ion exchange, dissolution, complexation, mineralization, precipitation, biological effects, and non-equilibrium dynamics) are involved in the migration process.

13. In many cases, both dredged material and soil have similar chemical and physical characteristics. However, distinct differences between the two materials occur in migration trends and constituent concentration levels. Variance in organic concentrations and redox conditions are most significant. In general, dredged material can be expected to have a higher organic content and a lower redox potential than a typical soil and thereby influence other chemical characteristics of the two materials, e.g., many species of trace metals are transformed to reduced states in dredged material, while oxidized species predominate in aerated soils.

14. Other differences between the concentration and chemical form of constituents in dredged material and soils are related to their environment: dredged material is removed from aquatic environments (saline, fresh, or brackish), while soils are generally subjected to constantly changing dry and wet cycles. Because of these differences in environment, microbiological activity and its effect on

the chemical kinetics and flux of constituents can be different.

15. Mineral constituents which are not subject to redox changes can also be different in dredged material and soil; soil, in many cases, contains more primary minerals and dredged material more secondary (weathered) minerals. Thus, the migration phenomena for constituents can vary greatly.

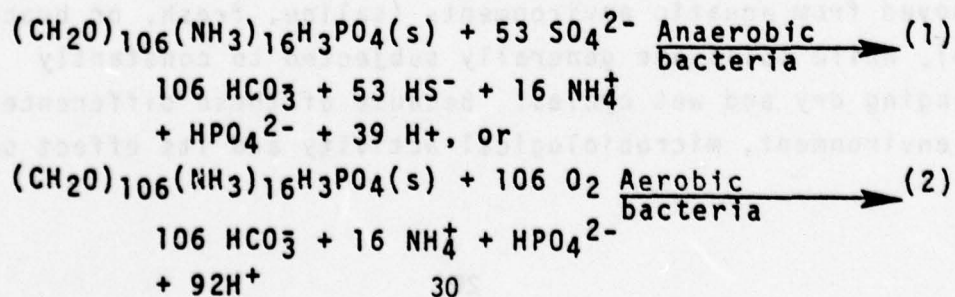
16. Due to the difference in characteristics of dredged material and soil, the discussion of the possible mechanisms involved in the migration of constituents will be divided into two sections: controlling mechanisms for the migration of constituents in (1) dredged material, and (2) in soil.

Controlling Mechanisms for Migration of Constituents in Dredged Material

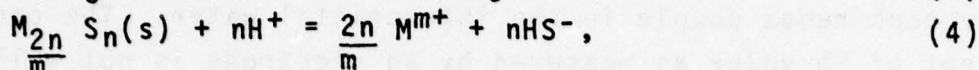
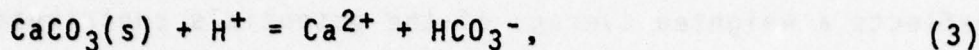
General parameters

17. The general parameters studied for determining controlling mechanisms were pH, Eh, TOC, and alkalinity. The pH levels of the interstitial water of dredged material are controlled by redox reaction, organic decomposition, dissolution or precipitation, and solid transformation (1, 2, 3, 4). These mechanisms for controlling pH can be expressed in the following general equations:

Redox reaction and organic decomposition: for example

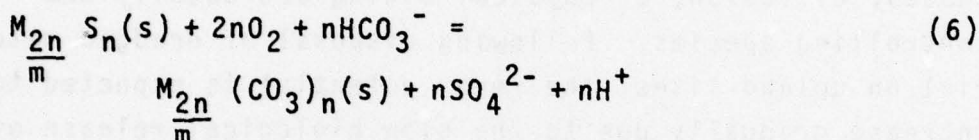
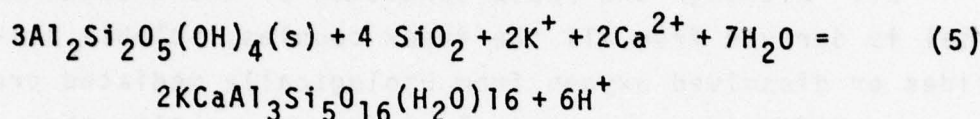


Solubilization: for example



(where $\frac{M_{2n}}{m} \text{S}_n$ represents metallic sulfides)

Solid transformation: for example



18. In general, oxidation will result in a lowering of pH levels while reduction will increase pH values. For example, the increase in carbon dioxide and hydrogen sulfide that results from oxidation of organic matter causes the lowering of pH levels in the interstitial water of polluted sediments (4). However, due to the presence of buffering solids in dredged material, the produced H^+ ion can be neutralized immediately.

19. Baas Becking et al. have shown that the pH of marine sediments is relatively invariable, values falling between 6.8 and 8.2 (5), although data on more than 1,000 samples of recent sediment indicate pH values ranging from 6.4 to 9.5 (6, 7). The model of Ben-Yaakov predicts a range of 6.9 to 8.3 for pH of interstitial waters of anoxic marine sediments (1).

20. In this study, redox potential (Eh) is important: it influences the oxidation state and chemical forms of virtually all the constituents in the dredged material-interstitial water system. Redox measurements of natural

waters are not specific for a single redox couple (8). Thus, measured redox potential is in reality a composite and reflects a weighted average of the potentials contributed by each redox couple in the interstitial water. The concept of Eh value as measured by an electrode is not well defined. However, the results are helpful in assessing whether the oxidation or reduction state predominates in the environment.

21. Although the redox condition of the dredged material is derived from all the redox couples, soluble sulfides or dissolved oxygen from biologically mediated processes, diffusion, or physical mixing are usually the controlling species. Following disposal of dredged material on upland sites, the redox potential is expected to increase gradually due to the slow biological release of soluble sulfides and relatively fast diffusion and mixing of dissolved oxygen. Numerous redox reactions can be expected during the redox changes by sulfide and oxygen. Table 1 lists some important related theoretical redox reactions in the dredged material-interstitial water system. In this table it can be seen that at pH 8, ferrous sulfide solid (FeS(s)) can be converted to ferric hydroxide solid ($\text{Fe(OH)}_3\text{(s)}$) at -447 mV, while at the same pH value, most of the manganous sulfide (MnS(s)) will be transformed to manganite (MnOOH(s)), when Eh is greater than +287 mV. Other redox reactions and corresponding Eh values can be found in the same table.

22. TOC in the leachates is important because the organics can form significant complexes with metals resulting in trace metal solubilization. Organic species also may change the redox conditions through biological degradation. After discharge of leachates into surface or subsurface receiving waters, the oxygen demand in the receiving waters can increase due to the elution of organic matter from the dredged material to the leachates.

23. The major mechanisms for the migration of TOC between dredged material and interstitial waters are bioconversion, hydrolytic reaction, surface sorption, and metal-organic reactions. Bioconversion can either decrease or increase TOC levels through microbial synthesis as well as microbial degradation of both soluble and solid organic matter. Over a long period of time, TOC behavior may be most strongly influenced by bioconversion mechanisms. Hydrolysis of organic material can increase TOC levels. Organics can also be released or taken up through surface sorption or by particles in dredged material, especially clay minerals, hydrous oxides, and noncrystalline materials (9). Chelation may take place either in solution or on particle surfaces. Specific chelates in the dredged material-leaching fluid system may include microbial slimes, gums, cell debris, humus, lignin polymers, polysaccharides, tannins, polyphenols, proteins, quinones, and substances with low molecular weights (aliphatic acids, amino acids, organic phosphates, phenolics, and volatile acid complexes). All these materials have an ability to complex soluble metals or insoluble particulates and regulate TOC levels.

24. Alkalinity of water is a measure of its capacity to neutralize acids. In general, alkalinity is due primarily to carbonates. Although dissolved silicates, borates, ammonia, organic bases, sulfides, and phosphates contribute alkalinity, these noncarbonate concentrations are small in comparison to the carbonate species. In the dredged material-leaching fluid system, alkalinity can be expressed as:

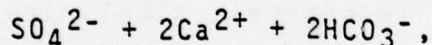
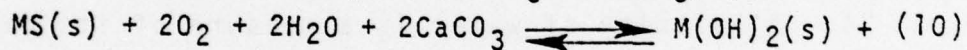
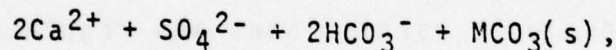
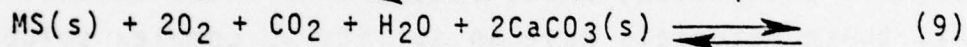
$$[Alk] = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [NH_3] + [SiO(OH)_3^-] + [OH^-] - [H^+] \quad (7)$$

25. Borate, silicate, and ammonia contribute little; the changes in alkalinity in any dredged material-leaching fluid system are primarily due to the changes in carbonate

species, including bicarbonate-carbonate ions. The main mechanisms involved are solubilization and solid transformation.

26. The dissolution/precipitation of metallic carbonate solids, such as calcite, dolomite, etc., in the dredged material-leaching fluid system, is usually caused by pH changes, mainly due to the release of carbon dioxide from dredged material, which change the solubility of the solids.

27. The solid transformation, especially of metallic sulfide solids (MS) to metallic carbonate (MCO_3), hydroxide (e.g., M(OH)_2 and M(OH)_3), oxide (e.g., MO), or silicate (e.g., MSiO_3) solids also can change the alkalinity in this experiment (10). With the exception of the conversions of metal sulfides, metal carbonate, or metal silicates, the dissolution of carbonate solids will also be involved. Some examples for solid transformation effects are (10):



Major ions

28. In this experiment, the major ions studied were sodium, potassium, calcium, magnesium, and chloride. The concentration of these ions is usually very high in the dredged material-leaching fluid system, because:

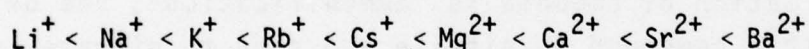
- The solubilities of simple solids of major ions are relatively high.
- The solubilities of clay minerals may be low enough to reduce the concentrations of major

ions. However, the nucleation of clay minerals is extremely slow.

- No other mechanisms can reduce the soluble levels.

29. Possible mechanisms for regulating the levels of major ions, i.e., solubilization and ion exchange, were mentioned above (11). Solubilization is significant only for calcium and magnesium. Calcite, aragonite, dolomite, and brucite regulate concentrations through solubilization. Other complex solids, due to the kinetic constraint, will not play important roles in precipitation/dissolution reactions.

30. Ion exchange is one of the important mechanisms for controlling the migration of major ions. Usually occurring on the surface of clay minerals and colloidal organics, the capacity of ion exchange is dependent upon the crystalline structure of the mineral and the chemical composition of the leaching fluids in contact with the mineral. Ion exchange in these minerals is a reversible chemical reaction which follows the law of mass action and is restricted by the number of exchange sites on the mineral and the strength of the bonding of the exchangeable ions to the mineral surface. The order of replaceability of the common cations has been found to be (12):



31. In dredged material-leaching fluid interfaces, the migration of the chloride ion due to ion exchange is possible, but has little effect (13). The chloride ion is negative, attracted only by the positive charge at the edge of the clay minerals. Since it has a much larger volume, the chloride ion cannot be replaced with either the oxygen or hydroxyl ions.

32. Dilution can be of greater importance than solubilization and ion exchange for the control of the major

ions, especially sodium, potassium, and chloride ions. The porosity of the dredged material and the flow rate of the leaching fluid may become significant factors in regulating the migration of these ions.

Nutrients-Nitrogen

33. The nutrients emphasized in this experiment were the nitrogen and phosphorus compounds. In most natural water systems nitrogen compounds include organic-nitrogen, ammonia-nitrogen, nitrite-nitrogen, and nitrate-nitrogen. The transformation of these nitrogen compounds is greatly affected by biologically mediated reactions which, in turn, are controlled by the types and population of micro-organisms, pH, redox conditions, and dissolved oxygen concentrations as well as the concentrations of the compounds themselves. Other mechanisms contributing to the transport of nitrogen compounds are diffusion, sorption, complexation, and hydrolytic reactions.

34. Biological reactions. All reactions carried out by living organisms indirectly require nitrogen. The cycle of nitrogen in the dredged material-leaching fluid system is shown in Figure 1. "Nitrogen fixation" is a process performed by a few bacteria and blue-green algae. "Mineralization" converts organic nitrogen into inorganic forms. The initial formation of ammonia is "ammonification"; the oxidation of this compound to nitrite and then to nitrate is "nitrification." The incorporation of ammonia or nitrate into biological tissue is "immobilization" or "assimilation." Combined nitrogen is ultimately returned to the atmosphere through "denitrification."

35. Organic matter in dredged material seems to play an important role in the reduction and fixation of nitrogen compounds. Most of the nitrogen in sediments is present as organic nitrogen which is only slowly released by the activity of the biotic community (14). Thus, the rate of

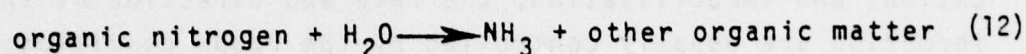
biodegradation of organic matter usually influences the flux of nitrogen. Many species of bacteria and fungi are capable of reducing organic nitrogen compounds, nitrate and nitrite; others can oxidize nitrogen compounds. All these reactions are enzyme-catalyzed and highly pH dependent.

36. Forms of nitrogen are greatly affected by biological effects, ammonification, nitrification, denitrification, and immobilization; the rate and direction of transformation are usually controlled by the redox conditions of the dredged material-leaching fluid system (15, 16, 17). Rittenberg et al. found that ammonia can be regenerated from sediments and oxidized to nitrate if the Eh value in the contacting water is positive (18). According to Austin and Lee, the concentration of ammonia-nitrogen will increase under anaerobic conditions and remain at low levels under aerobic conditions (19). Nissenbaum et al. reported that ammonia-nitrogen reached a concentration of 250 ppm under reducing conditions in the interstitial water of a fjord in British Columbia, but that it could not be detected in the overlying water column (20). Moreover, in one unusually well-oxidized core sample (the redox potential ranged from +340 to +380 mV, a nitrogen-oxidizing environment), no ammonia-nitrogen could be detected. Patrick; and Bailey et al. have shown that nitrate is reduced by denitrification when the Eh drops below approximately 340 or 225 mV at pH 5 or 7, respectively (21, 22).

37. In this experiment it was calculated that ammonia-nitrogen (mainly as ammonium species) could be oxidized to nitrite at +349 mV at pH 7 and +268 mV at pH 8 (Table 1). One can also see that ammonia-nitrogen can be oxidized to nitrate when the redox potential is higher than +369 mV at pH 7 or +294 mV at pH 8. Nitrite-nitrogen is relatively

unstable and can be converted to ammonia or nitrate very easily, depending upon the environmental conditions. The pH value can also affect the rate.

38. Hydrolytic reactions. Hydrolytic reactions also transform nitrogen compounds (e.g., ammonia is formed by the hydrolysis of organic nitrogen, as shown in the following equation (16):



39. Sorption reactions. Due to its cationic nature, ammonia-nitrogen (chiefly in the form of ammonium) may be adsorped onto solid materials by ion-exchange reactions with mineral or organic matter in the dredged material. Adsorption is considered one of the most important mechanisms for controlling movement of ammonia-nitrogen through soils and, depending upon the soil environment, might even override biological action (23). The nitrate anion is relatively mobile and not retained by ion-exchange processes.

40. Complexation reactions. Under many circumstances, nitrogen compounds can be complexed with metal ions (24). As calculated by Lu, only some 9 percent of ammonia in seawater exists as free ammonia (10). The remainder is in the form of metal-ammonia complexes ($\text{Hg}(\text{NH}_3)_2^{2+}$, $\text{Hg}(\text{NH}_3)^{2+}$, $\text{Cu}(\text{NH}_3)^{2+}$, $\text{Cu}(\text{NH}_3)_2^{2+}$, $\text{Ni}(\text{NH}_3)^{2+}$, $\text{Ni}(\text{NH}_3)_2^{2+}$, $\text{Cd}(\text{NH}_3)^{2+}$, $\text{Zn}(\text{NH}_3)^{2+}$, etc.). On the other hand, in seawater, 93 percent of the nitrate remains as the free anion; the remainder is in NaNO_3^0 , $\text{Ca}(\text{NO}_3)^+$, and KNO_3^0 complexes. The relative importance of metal-organic nitrogen complexes is not completely understood.

41. There is little information on organic nitrogen species and the thermodynamics of complex formation. However, from data on the complexation of trace metals with humic substances and amino acids (10), it can be surmised

that organic nitrogen can also complex with trace metals to a great extent, depending on the concentration of metals.

42. This complexation increases nitrogen levels in solution. The importance of the resulting nitrogen complexes depends upon the types and levels of metals and the formation constants, activity coefficients, and pH levels of the leaching solutions in contact with the dredged material.

43. Diffusion reactions. Diffusion of nitrogen species across the interface of dredged material and leaching solution can be accelerated by the continuous removal of nitrogen compounds by the leaching fluid which will increase the concentration flux. Engler and Patrick; Kemp and Mudrochova; and Graetz et al. suggest that the diffusion of interstitial dissolved ammonia-nitrogen into the thin oxygenated surface sediment horizon or across the sediment-water interface is an important source of ammonia-nitrogen-nitrate-nitrogen in the water column (25, 26, 27). Because of this process, complexation may also perhaps be increased. Since the diffusion rate is controlled by the concentration gradient, the flow rates of leaching fluids and the dilution of interstitial water will become important factors in regulating diffusion reactions.

Nutrients-Phosphorus

44. The transport of phosphorus compounds in the dredged material-leaching fluid system is a complex of chemical, biochemical, and physical interactions; the most important are solubilization, sorption, and biological effects.

45. Solubilization effects. Precipitation and dissolution of the iron, aluminum, and calcium phosphates in sediments are considered the major mechanisms regulating the levels and directions of phosphate transport in sediment-water systems. To understand the importance of

solubilization effects, phosphate solids possible in dredged material have to be assessed. The phosphate minerals known to exist in sediments are strengite (FePO_4), variscite (AlPO_4), vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), anapaite ($\text{Ca}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$), hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), wavellite ($\text{Al}_3(\text{OH})_3(\text{PO}_4)_2$), mixed phosphate solids (such as clay-phosphate), and organic phosphorus (28, 29, 30, 31). Among these, only a few solids of iron, aluminum, and calcium phosphate can control the level of phosphate through solubilization. In acidic sediments, iron and aluminum phosphate solids are considered the most stable; in neutral and alkaline sediments, calcium phosphate predominates (32). Frink suggests an overall shift from aluminum phosphate to iron phosphate in acid soils, but in the neutral lake sediments, a conversion of aluminum phosphate to calcium phosphate (33).

46. The transformation of most of the stable solids is greatly affected by environmental conditions, such as the pH and Eh levels in the interfacial or interstitial waters. Nriagu and Dell reported that for pH values from 6.5 to 9, where redox potential ≤ 0 mV, vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) is the most stable phosphate mineral (29); the requirements for strengite (FePO_4) formation include a high redox potential, large phosphorus concentrations, and low pH.

47. The formation of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) in sediments also has been suggested (34, 35, 36). However, Nriagu and Dell; and Lee suggested that anapaite rather than hydroxyapatite would be the stable calcium phosphate solid. If calcium or aluminum phosphate solids are dominant, the pH effect becomes very significant (29, 37). However, if the controlling solid is iron phosphate, either pH or Eh could affect the transport of phosphate

significantly. In a typical natural sediment water system, the release of phosphate is usually caused by the reduction of the ferric phosphate solid to the more soluble ferrous solid with a resulting increase in phosphate concentration in solution.

48. Sorption. Inorganic phosphorus can be sorbed by a variety of solids in sediments: oxides and hydrous oxides of iron and aluminum, calcium carbonate, and clay minerals, e.g., kaolinite, montmorillonite (30, 33, 38, 39, 40, 41, 42, 43, 44). This sorption is usually influenced by pH, redox potential, and the concentration of such ions as bicarbonate in the system.

49. Although sorbed rapidly at first, additional inorganic phosphorus sorption occurs at a much slower, diffusion-controlled rate (45). Generally, the adsorption of inorganic phosphate follows the Freundlich and Langmuir adsorption isotherms, the Freundlich equation for the high phosphorus concentrations, the Langmuir equation for low phosphorus concentrations (46).

50. Biological effects. The biological incorporation of dissolved inorganic phosphorus into soluble organic phosphorus and the subsequent settling of the insoluble solid has been reported as one of the important mechanisms for removing phosphorus from surface water (30). However, it is suggested that this phenomenon occurs only in the field situation where vegetation is growing. Under laboratory conditions, the main biological effects on phosphorus may come from the biodegradation of organic-phosphorus into the water. The equations for these reactions have been given earlier in this report.

Trace metals

51. The movement of trace metals between interfaces of dredged material and leaching fluids is extremely complex. Not only are there numerous controlling factors,

but many unknowns beyond present state-of-the-art knowledge are involved. Thermodynamic and kinetic influences make transport phenomena difficult to explain and predict. Some of the major mechanisms that influence mobility of trace metals in solid-liquid interfaces are:

- Solubilization
- Solid solution
- Sorption
- Complexation
- Bioreaction
- Dilution.

Each of these mechanisms may exert some influence on the mobilization of trace metals into solution from dredged material and the consequent migration of trace constituents into groundwaters underlying upland dredged material disposal sites.

52. Solubilization effect. The most important effect of solubility on the mobilization of trace metals is the solid form of the metal. For any given metal (M) and its controlling solids M_pL_q , the following generalized relationship has been demonstrated to exist:

$$[M_f] = \left(\frac{(K_{sp})M_pL_q}{\gamma_M^p \gamma_L^q [L_f]^q} \right)^{1/p} \quad (13)$$

where $[M_f]$ = concentration of free metal ions,
 $[L_f]$ = concentration of free ligands,
 γ = ion activity coefficient,
 K_{sp} = solubility product, and
 p, q = positive integer

Depending upon the redox conditions and ligands that occur in the solution, a number of solid metal species exist for any given trace metal. A compilation of the common solid species of trace metals in the sediments is shown in

Table 2, while the solubility products of some of the important solids are listed in Table 3.

53. In general, in reducing environments (such as in the in situ dredged material), metallic sulfide species will predominate, while under oxidizing environments (such as in leaching with aerobic fluids), they gradually may be converted to carbonate, hydroxide, oxyhydroxide, oxide, or silicate solids (43). As a result of these phenomena, the solubility and consequent potential for mobilization of trace metals changes. When the reducing dredged material is oxidized, the solubility of cadmium, copper, lead, and zinc may increase, since higher solubility solids have been formed. The solubility of iron and manganese may, however, decrease due to the formation of high oxidation states, lower solubility oxides, or hydroxides (47).

54. Solid solution effect. Pure solids seldom occur in nature. Isomorphous replacement by a foreign constituent in the crystalline lattice is an important factor by which the activity of the solid phase may be decreased. The solid solution effect may be important in regulating free trace metal ion concentrations in solid-liquid interfaces, especially in an oxidizing environment, where several metallic species of a particular trace metal can coexist together. When the solid solution effect is prominent, the basic trends of solid transformation and the relative ratio of all coexisting solids may govern the solubility of a particular metal. These phenomena are extremely complex and not at all understood (28).

55. Sorption effect. The interfacial association between trace metals and dredged material particles is another important process in regulating the concentration of metals in the leaching fluid of dredged material. The abundance of sulfides, oxides, hydroxides, organic matter, and clay minerals in the dredged material is the primary

controlling mechanism for the sorption mechanisms of trace metals (48, 49, 50). Types of solids, pH values, and the presence of other soluble ions can affect the sorption process of any particular trace metal ion. Definitive information on the sorption effect for dredged material water systems is sparse.

56. Complexation effect. Metallic complex formation may be the most significant factor for adjusting the total metal concentrations in solid-water interfaces (10, 47). For any given metal M and its complexation ligands L(i), the concentration of complex species can be expressed as:

$$[M_m L(i)_n] = m \beta(i)_{nm} [M_f]^m [L(i)_f]^n \quad (14)$$

$$\frac{\gamma_M^m \gamma_{L(i)}^n}{\gamma_{M_m L(i)_n}}$$

where $[L(i)_f]$ = free concentration of ith ligands

n, m = composition of the complex

$M_m L(i)_n$

$\beta(i)_{nm}$ = overall formation constant of complexes $M_m L(i)_n$

Therefore, the total concentration of soluble trace metals $[M_t]$ can be derived as follows (generally multisalt ligands are negligible and are omitted in this equation):

$$[M_t] = [M_f] + m \sum_{n=1}^k \sum_{i=1}^j [M_m L(i)_n] = \quad (15)$$

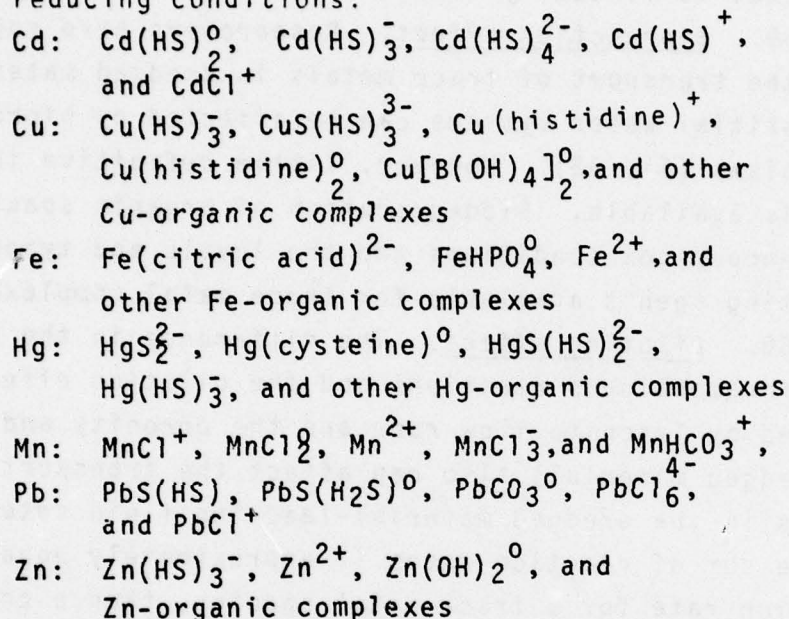
$$[M_f] + m \sum_{n=1}^k \sum_{i=1}^j \beta(i)_{nm} [M_f]^m [L(i)_f]^n$$

$$\frac{\gamma_M^m \gamma_{L(i)}^n}{\gamma_{M_m L(i)_n}}$$

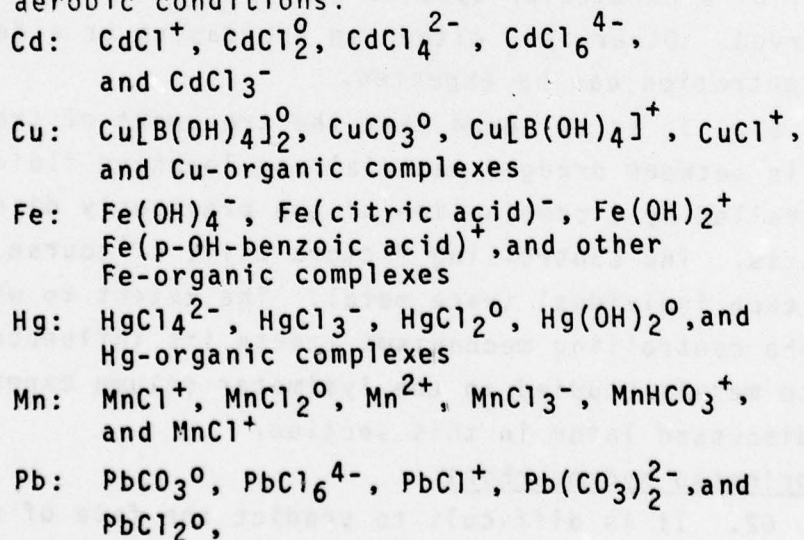
In order to solve the above equation, additional data such as ligand species, overall formation constants, activity coefficients, and free ion concentration are needed.

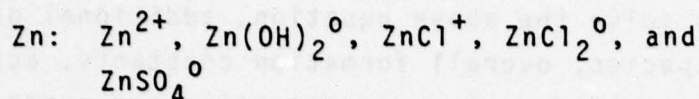
57. Lu suggests that the major complexes of trace metals in the interfaces of sediment-seawater systems are as follows (10, 47):

Under reducing conditions:



Under aerobic conditions:





58. Because of the many unknown organic species and lack of knowledge concerning thermodynamic data in the dredged material, a precise evaluation of all the metallic complexes is virtually impossible.

59. Bioreaction effect. Researchers have suggested that the transport of trace metals in dredged material-interstitial water systems can be affected by bioreaction mechanisms (51, 52). However, little definitive information is available. Biodegradation of organic species can influence redox conditions and the levels and types of chelating agents available for trace metal complexation.

60. Dilution effect. The difference in the rates of the aforementioned reactions and the dilution effect (controlled by leachate flow rate and the porosity and volume of dredged material) also can affect the transport of metals in the dredged material-leaching fluid interfaces. If the sum of reaction rates is approximately equal to the dilution rate for a trace metal species, then a constant level of a particular species in relation to time can be observed. Otherwise, either an increasing or a decreasing concentration can be expected.

61. It is believed that the transport of trace metals between dredged material and leaching fluids is controlled by a combination of the previously discussed effects. The controlling factors will, of course, vary for each individual trace metal. The extent to which each of the controlling mechanisms exerts its influence on the trace metals studied in the lysimeter column experiments is discussed later in this section.

Chlorinated hydrocarbons

62. It is difficult to predict the fate of chlorinated hydrocarbons in the environment. In general,

volatilization, microbial degradation, chemical hydrolysis, oxidation, ultraviolet decomposition, and sorption can be involved (16, 53, 54, 55, 56, 57). In the dredged material-leaching fluid system, sorption might be dominant.

63. Previous studies have shown that chlorinated hydrocarbons tend to be strongly sorbed by sediments (16, 53, 58, 59). Although these compounds are present in some sediments in large amounts, little release would be expected to occur because of the strong sorption affinity of both organic and inorganic solid materials in sediments. As suggested by the references, the major adsorbents for chlorinated hydrocarbons in sediment are clay minerals, iron and manganese hydrated oxides, and organic material, including oil and grease. Adsorption is accomplished chiefly by the formation of hydrogen bonds, as well as some other reactions, e.g., physical adsorption as caused by van der Waals interparticle attraction.

Controlling Mechanisms for Migration of Constituents in Soils

64. When dredged material is disposed in upland sites, the many chemical, physical, and biological reactions occurring in the underlying soils may affect the mobilization and attenuation of the various constituents from the disposed dredged material. This complex series of reactions will influence, to a great extent, the movement of contaminants from the dredged material into affected groundwater systems. The following concepts are important in the migration of trace constituents in leaching solutions from soil:

- Attenuation by soil due to soil properties
- Attenuation by soil due to the chemical compositions of soil leachates
- Mobilization by soil due to soil properties
- Mobilization by soil due to the chemical compositions of dredged material leachates.

65. Many complex mechanisms influence and control the attenuation and mobilization of trace constituents in soils. Soil is a dynamic chemical, physical, and biological system which may transform constituents into other forms. Some of the constituents in dredged material leachates, when passed through soils, may interact with the soil system while others may pass through virtually unchanged into underground water sources. Numerous reactions may occur when trace constituents in leaching solutions interact with soils, including:

- Formation of precipitates
- Attachment to soil particulates
- Formation of organic and/or inorganic complexes
- Conversion to other chemical species by biological processes
- Movement through the soil unchanged.

66. Although these reactions can be grouped as above, clear distinctions cannot always be made. Moreover, a factor which may mobilize or attenuate a constituent in one soil may have no effect in another soil; a factor which may inhibit movement of one element may have no influence on the movement of another element. Before discussing the behavior of each individual constituent in soil systems, a general discussion on the possible phenomena which may affect the migration of constituents in soils is necessary. Each of the preceding phenomena is discussed in relation to the effects on the chemical, physical, and biological mechanisms where applicable.

Chemical mechanisms

67. pH effects. As mentioned, the pH of a soil/water system will influence the direction of the alteration processes (precipitation, dissolution, redox reaction, and sorption) and will affect the speciation of almost all the constituents in the systems. In general, the acid pH

conditions in systems will affect the migration and attenuation of chemical constituents as follows:

- Soils will tend to sorb less constituents.
- Soils will tend to exchange more exchangeable constituents.
- More solids (oxide, hydroxide, and carbonate species) will dissolve from solids.

With some exceptions, if the pH levels of the soil system are decreased by influents, the attenuative capacity of the soil system itself will be decreased.

68. Redox effects. The redox potential of any given soil/water system will affect the valence and chemical forms of many constituents in the system (Table 1). Redox reactions in the interfacing soils of the experiment are most likely initiated by the biological activity in dredged material and soil as well as by diffusion of oxygen, from the atmosphere. Due to the biological reactions and continuing diffusion of oxygen, redox equilibrium probably could not be reached. In general, after disposal of dredged material on an interfacial soil, the redox potential of the soil system will be decreased due to the basic reducing nature of dredged material. Owing to this redox change, the migration and attenuation of constituents will be greatly affected. For example, the oxidized metallic solids in soil can be changed gradually to more reducing metallic solids and consequently affect the solubility of these solids, affecting the precipitation/dissolution reactions. Differences in redox potentials can also alter the sorption reaction because of redox effects on solid transformation.

69. Precipitation and dissolution effects. Solubilization (precipitation/dissolution) is important in the control of levels of soluble constituents; the migration trends of constituents are usually toward the equilibrium state, which is likewise controlled by the solubilities of solids.

70. Adsorption effects. Adsorption is probably the most important process influencing the attenuation of the trace constituents in soils. Under oxidizing conditions, adsorption usually can regulate the concentration of a constituent well below the level controlled by precipitation/dissolution effects. The high anion retention by soils that cannot be attributed to anion exchange or precipitation can usually be explained by adsorption (49). Adsorption processes can take place rapidly. Because the nucleation of a solid is usually very slow, the adsorption mechanisms may still affect the concentration of a constituent even if that constituent has a low solubility controlling solid. The coprecipitation of a constituent as an impurity in solid phase accumulations and crystal structures is common in nature. Since it is extremely difficult to separate the effects of coprecipitation and adsorption, both are usually included as adsorption. Some of the most important adsorption mechanisms in soils are those associated with iron and manganese hydroxides and hydroxy oxides (49). A small quantity of hydrous oxide solids can create a large reactive surface. In addition to iron and manganese hydrous oxide solids, clay minerals and soil-organic solids may also adsorb constituents from the solution phase of soil/water systems.

71. Complexation effects. Complex formation may have two different effects on the migration and attenuation of constituents. In the solution phase, it can greatly increase the concentration of constituents. On the other hand, if the complex formation is between the soluble constituents and solid surfaces, especially organic chelates, then the levels of constituents can be decreased. Since both soil and dredged material contain a wide variety of organic compounds and complexes, the net attenuation or migration is often difficult to evaluate.

72. Ion exchange effects. Most of the ion exchange effects in soil/water systems originate from the exchange sites on layered silicate clays and organic matter. In general, the layered aluminum-silicate secondary minerals in soils hold a permanent negative charge. Ion exchange effects, therefore, are much more important to the migration of positive charged ions than to negative charged ions. The total capacity of soils to exchange cations is called the cation exchange capacity (CEC); the CEC of any particular soil is affected by the kind and quantity of clay mineral and organic matter and the pH of the soil/water solution. For the three predominant types of clay minerals, CEC values exist in the following order:

montmorillonite > illite > kaolinite

73. Soil textures greatly affect CEC values. Generally, soils containing smaller particles have higher CEC values. Soils high in organic material also tend to have higher CEC values than soils with less organic material. The cation exchange capacity of soils increases with increasing soil pH. The removal of trace metals from soil-water interfaces by cation exchange is usually insignificant when compared to other mechanisms; common cations, calcium, magnesium, potassium, and sodium are usually present in higher concentration than any of the trace metals such as cadmium or zinc. Consequently, trace metals cannot successfully compete for the cation exchange sites that are dominated by the common cations (60).

Physical mechanisms

74. Straining effects. Solid particles in solutions generally range in size from $0.001\ \mu$ to $8\ \mu$. The removal of constituents by the filtering action of soils is applied to a wide range of particle sizes, not just to the

larger particles. Another straining effect by soils is the attenuation of nonpolar organic compounds (such as oils, grease, and hydrocarbons of lower molecular weight). Even a small depth of soil can remove a large quantity of such material.

75. Solution flux effects. Due to decreased permeabilities, the finer the soil texture the more slowly leaching solutions tend to flow. The degree of attenuation by soils is not influenced only by solution flux or flow rate. If other influencing factors remain unchanged, lower solution flux means longer contact time in which the reaction between the soil particles and the dredged material leachates can occur. Solution flux may also be affected by pore size and soil particle-size distribution. If solution flux is too high, scouring may take place, i.e., particulate forms of constituents can be washed out by the leaching solutions.

76. Diffusion and dispersion effects. Diffusion mechanisms can affect the migration and attenuation of constituents in soil/water systems in several ways. Diffusion of atmospheric oxygen to the soil system can affect the redox potential of the soil system. In the case of very low leachate flow rates, diffusion of soluble species in the soil solution may be a significant migration mechanism. The migration of nonreactive solutes by a phenomenon described as "dispersion" can be greater than that attributable to solution flow rate (61, 62, 63). It is generally very difficult to separate the effects of diffusion and dispersion mechanisms.

77. Physical sorption effects. The effects of physical adsorption are not well defined and are difficult to distinguish from chemical adsorption. It is generally suggested that physical sorption is relatively weak and reversible, while chemical sorption is much stronger and

irreversible. As mentioned by Fuller, only a small proportion of the reactions of trace metals in soil/water solutions can usually be defined as physical adsorption (60). The remainder can be accounted for by chemical bonding or chemical adsorption.

Biological mechanisms

78. The effects of soil bacteria, fungi, actinomycetes, algae, protozoa, earthworms, etc., on the chemical states of various constituents in soil/water systems are numerous. Biological reactions affect many chemical reactions including oxidation/reduction, mineralization, immobilization, precipitation, and complexation, but most important are the effects on oxidation/reduction reactions and the transformation of organic species.

79. Oxidation/reduction reactions are greatly affected by the degradation of organic compounds in soil. The mode of degradation not only changes with the species of organism, but it also may affect the redox potential and thus the oxidation state and chemical forms of all constituents in both solution and solid phases of the soil systems.

80. Through mineralization, trace elements, plant nutrients, organic chemicals, microbial tissues, and organic-inorganic complexes may be converted into inorganic states. Through biological assimilation, the inorganic nutrients and trace metals may be transformed into microbial tissue, thus biologically immobilizing these constituents.

81. Organic complexes which accumulate in soils as a result of both microbial synthesis and degradation have a high capacity to combine strongly with trace metals and other constituents. Through these reactions the constituents in soil systems can be mobilized, complexed, precipitated, or sorbed.

PART III: EXPERIMENTAL METHODS AND MATERIALS

Introduction

82. The overall objective of this study was to examine several possible permutations of different field environmental conditions, types of dredged material, interfacing soils, and leaching fluids and to ascertain their effects on the quality of the leachate produced when dredged material is disposed in upland areas.

83. A wide range of laboratory conditions had to be selected to simulate potential field environments. Design criteria and experimental methods were developed through the following:

- Literature review of environmental simulations
- Lysimeter column design
- Experimental materials selection; and
- Experimental procedures formulation.

Literature Review of Experimental Simulation

84. To assess the potential impact of dredged material leachates on groundwater and surface waters, a laboratory design to simulate the physical and chemical environment of upland disposal areas was necessary. This design was to include environmental variables (rainfall contacting the dredged material, groundwater inundation, acid rainfall) as well as leachate drainage, varying dredged material and soil characteristics, and other factors which may affect the quality of leachate produced, or the movement and concentration of trace contaminants within the dredged material.

85. One requirement for experimentation was that the construction materials necessary for any laboratory apparatus would have to interact minimally with constituents

contained in the dredged material, interfacing soils, and leachates.

86. With these constraints in mind, pertinent literature was examined. Three basic experimental designs to measure the movement of trace constituents in soil were found:

- Tension plates
- In situ lysimeter columns, and
- Laboratory lysimeter columns.

A discussion of each follows.

Tension plates

87. Tension (drainage) plates are usually inserted at varying depths in the soil; they are used to measure movement of water and ionic species as influenced by slope, crop grown, and moisture contents. Samples removed from the plates can be analyzed for any of the specified parameters. A partial listing of research projects using tension plates is given in Table 4.

88. Since a tension plate setup requires field installation of the plates and extensive pretesting to establish the environmental conditions specified in the experiment, the use of tension plates appeared to be impractical for the current study.

In situ lysimeter columns

89. In situ lysimeters, installed in the field and for the most part fabricated from steel, have been used in the past to study salt accumulation and ion movement in soils, leachate quality, and evaporation as well as other parameters associated with evapotranspiration. Table 5 presents a partial listing of these systems.

90. In situ experimental setups are extremely costly, requiring large fields, considerable excavation and numerous replicates. Moreover, very little control can be exerted on the environmental variables.

Laboratory lysimeter columns

91. Laboratory lysimeter columns were the last experimental system examined and provided the greatest variety of design. Experiments reviewed ranged from examination of evaporation loss of soil water to developing models of ion movements in soil.

92. Table 6 lists some of the laboratory lysimeter column experimental designs examined in the literature review. Obviously, each design was developed for a unique experimental condition.

93. Most laboratory lysimeter setups offer: 1) control over the input and output of a constituent under experimental conditions, and 2) frequent and effortless observation and monitoring of the progress of an experiment.

94. Environmental variables which can be controlled in the laboratory include:

- Ambient temperature
- Relative humidity
- Atmosphere above the lysimeter column
- Quality and amount of influent introduced
- Quantity of a given constituent added, and
- Amount of leachate collected.

Simulated environmental conditions can include alternate wetting and drying cycles, soil types, and plant species.

95. As previously discussed, field lysimeter designs are limited due to available land, economics, and the changing conditions of the surrounding environment of the experiment. However, it is possible to control temperature, evaporation, light, and extraneous foreign materials in laboratory lysimeter columns. Since it was necessary to use several dredged material and soil types and to control the variables mentioned above, laboratory lysimeter columns were selected for the subject experiment.

Lysimeter Column Design

96. A schematic of the laboratory lysimeter columns developed for the study under discussion is shown in Figure 2. The column walls and base were constructed of Plexiglas, minimizing interactions between the column and the experimental materials. Black plastic sheeting was wrapped around the columns and leachate collection hoses to eliminate light penetration and prevent algal growth. Polypropylene beads placed in the bottom of the columns prevented soil particles from migrating into the leachate collection bottle.

97. Sixteen columns, consisting of two soils and five types of dredged material were used. The columns were packed with moist soil to a depth of 30 cm (12 in.) and 30 cm (12 in.) of the dredged material was placed on top of the interfacing soil (Figure 3). No dredged material was used in the soil blank column.

98. The columns were housed in a temperature controlled room. Measured amounts of influent were added at the top of the column. The leachate flowed by gravity through tygon tubing into the leachate collection bottles which were kept under anaerobic conditions by a constant nitrogen gas purge and waterlock seal (Figure 3).

99. To minimize biological action, the bottles were placed in small insulated styrofoam boxes with chemical refrigerant and ice. The boxes permitted daily change of refrigerant and daily measurement of volumes of leachate.

100. Within the constraints of dredged material and soil permeabilities, the rate of leachate flow could be controlled by adjusting the height of each individual leachate collection bottle rack on the back of the lysimeter column stands (Figure 3).

Experimental Materials Selection

101. To simulate different environmental conditions and to provide an insight into the complex chemical, physical, and biological changes that may occur when dredged material is disposed in upland areas, different types of dredged material, interfacing soils, and leaching solutions were used in the experiment. Actual dredged material from a variety of geographical areas was used in the columns to enhance the applicability of the experimental results.

102. The sites from which the dredged material samples were obtained had been in use for some time. Bulk analysis of sediments had revealed high levels of certain constituents, high concentrations of at least some trace contaminants, and a wide range of salinities (from fresh water to brackish to saline). A "worst case" condition was, therefore, provided for the experiment.

103. The locations of the sites selected and the reasons for their selection are delineated in Table 7. A more detailed description of the physical and chemical parameters of each dredged material is included in the "Results and Discussion" section of this report.

104. Soils selected for use in the experiment were chosen to evaluate the attenuative capacities of two soils with different organic contents. The Lake Arrowhead sandy loam has a relatively high organic content while the Perkins loam soil is significantly lower in organic content (Table 8). The two soils also have different permeabilities, the permeability of the Lake Arrowhead sandy loam being significantly higher than that of the Perkins loam. The physical and chemical characteristics of the interfacing soils are discussed more fully in the "Results and Discussion" section of this report.

105. In this experiment, leaching solutions of varied chemical composition were selected to simulate the

many environmental conditions that may be expected to occur in various dredged material upland disposal areas. The solutions were as follows:

| <u>Leaching Fluid</u> | <u>Description</u> |
|-----------------------|--|
| Rainwater | Ultrapure distilled water |
| Acid rainwater | Ultrapure distilled water adjusted to pH 4.5 with SO ₂ gas |
| Fulvic acid solution | Fulvic acid (75 ppm) |
| Groundwater | 10 ⁻³ M NaHCO ₃ and 10 ⁻⁴ M CaCl ₂ with the solution buffered to pH 6 with CO ₂ gas |
| Landfill leachate | Actual sanitary landfill leachate |

106. These solutions were used to examine the different release and sorption mechanisms of contaminants in the dredged material/interstitial water interface and in the soil/dredged material leachate interface. Acid rainwater was used to simulate the "acid rains" prevalent in the eastern United States to determine if the depressed pH levels would mobilize more contaminants into solution than would other rainwaters. A fulvic acid solution was used to simulate natural organic-metallic chelation. Often upland dredged material disposal sites contain an abundance of dead and decaying organic matter; fluids flowing through soils in these areas may contain appreciable quantities of organic acids.

107. A groundwater simulating solution was used to develop "groundwater intrusion" conditions in one of the leachate lysimeter columns. Hardness and alkalinity were produced by adding sodium bicarbonate and calcium chloride to ultrapure distilled water. Leachate from an actual sanitary landfill was selected as a leaching fluid in one of the experimental columns to determine whether the myriad of organic complexing agents existing in municipal leachates

can increase trace metal mobilization by the formation of metal organic chelates. A more detailed discussion of the chemical constituencies of all the leaching solutions may be found in the "Results and Discussion" section of this report.

Experimental Procedures for Equipment Used in the Field and Laboratory

108. The procedures developed for use in this project, as well as existing methodology that was utilized, can be divided into the following subject areas:

- Cleaning procedures
- Procurement of experimental samples
- Introduction of interfacing soils to lysimeter columns
- Introduction of dredged material to lysimeter columns
- Removal of interfacing soils and dredged material from lysimeter columns
- Lysimeter column operations, and
- Analytical procedures.

The preceding topics form the basis for the following discussions on the experimental methods utilized throughout the course of the project.

Cleaning procedures

109. Because extremely low constituent levels were anticipated in the leachate, utmost care was taken in cleaning and preparing all field equipment, test columns, and laboratory apparatus. The following cleaning methods were used:

- a. Before soil and dredged material were placed in a lysimeter, each column was filled with tap water, scrubbed with a bristle brush to remove dust and debris that may have accumulated during construction and storage, and rinsed with tap water.

- b. Each column was thoroughly rinsed with distilled water, set up in its proper experimental configuration (Figure 3), and completely filled with a 5 percent hydrochloric acid solution.
- c. The hydrochloric acid solution was drained at the end of 48 hours and the columns thoroughly rinsed twice with distilled water and three times with ultrapure (18 megohm) water.

110. After the final rinsing, each of the columns was completely wrapped with six mil black polypropylene sheeting to prevent light penetration. This sheeting was kept on the columns throughout the course of the experiment to prevent algal growth.

111. All laboratory equipment, utensils, tubing, etc., were cleaned in a similar manner to prevent contamination; after final rinsing all materials and utensils were wrapped in parafilm sheeting until used.

Procurement of experimental samples

112. Representative samples of dredged material and interfacing soils were obtained in the field. In general, the dredged material samples had high moisture contents and could be considered flooded soils: there was an indication of intense reducing conditions in the samples as indicated by either a dark-gray or black color and/or associated sulfide odor. Extreme care was taken to transfer the dredged material from the various field locations to the laboratory in an unaltered state. Care was taken to eliminate the introduction of extraneous trace contaminants to the dredged material and interfacing soils from sampling equipment and other sources or due to the leaching of these contaminants into solution. The accuracy and care exercised in the sampling, preservation, and shipment of both dredged material and upland soils was emphasized since the experimental results were directly dependent upon careful adherence to prescribed procedures.

113. Prior to each field sampling trip, all necessary sampling materials were packaged and shipped to the sampling location. The sampling materials required are listed in Table 9.

114. All materials and equipment that were to come into contact with the dredged material/soils were meticulously cleaned to remove all trace contaminants. These procedures consisted of a 24-hr soaking in a 5 percent hydrochloric acid solution, followed by two rinsings with distilled water. The sampling materials were then rinsed three times with ultrapure (18 megohm) water. All the sample containers (buckets and lids), plastic trash can liners, and other materials that could contact the dredged material or soil were treated in this manner. Trash can liners were placed in a prepared bucket; the lids were placed on top of the buckets in a manner that would not engage the hermetic lid locks but would keep out all airborne contaminants until the buckets were used. The prepared buckets were then placed in clean plastic bags prior to shipment to the site.

115. Careful sampling procedures were followed when dredged material samples were obtained from existing upland disposal sites. The dessicated crust of the dredged material was broken with the shovel, removed, and discarded. The shovel head was then covered with two prepared (acid-washed) trash can liners. The split garden hose was placed over the edges of the shovel to prevent the plastic bags from tearing, and the plastic bags were fastened securely to the shovel handle with several rubber bands. The underlying dredged material was mixed thoroughly to ensure a homogeneous representative sample. The same procedures were used to obtain interfacing soil samples; the only difference was that approximately 5 cm (2 in.) of the upper soil layer was discarded prior to sampling.

116. The prepared buckets were filled to the brim with dredged material. An extremely small amount of slurry from the sampling area was added to each bucket so that it overflowed when sealed, eliminating to the extent possible any trapped air. Proper care was taken to ensure that all sample buckets were sealed tightly. This was accomplished by field personnel standing on the bucket lid until the locking rim was sealed. The bucket was placed in a plastic trash can liner and the bag sealed. Each packing carton was lined with three trash can liners; the sample bucket (sealed in a trash can liner of its own) was placed in the shipping box, the remaining space filled with frozen blue ice, and the three trash can liners individually sealed with baling wire. Fiber packing tape was used to seal the preaddressed corrugated shipping cartons, which were shipped via air freight to the SCS laboratory in Long Beach, California.

117. Soil samples were shoveled into acid-washed buckets, and the lids were securely sealed. The samples were shipped to the SCS laboratory in Long Beach without preservation by chilling.

Introduction of interfacing soils to lysimeter columns

118. To prevent migration of soil particles and to induce drainage from the lysimeter columns into the leachate sample collection bottles, a polypropylene mesh screen and a 5-cm (2-in.) layer of polypropylene beads were placed between the base of the column and the interfacing soil (Figure 3). The weight of the beads added to each column was recorded.

119. When interfacing soils were added in slurry form, it was found that the beads floated in water; it was impossible to maintain a distinct interface between the beads and the soil. Thereafter, the soil was thoroughly

mixed and added to the columns in dry form, in increments of 2-1/2 to 5 cm (1 to 2 in.), by sprinkling it evenly over the column bottom. To saturate and compact the soil, ultrapure distilled water was repeatedly applied with a polyethylene squeeze bottle until the soil reached 30 cm (1 ft) in height. This method was found to provide excellent compaction and a minimum of trapped air pockets. Weights and volumes of soils were recorded, and representative samples of saturated soil were taken of each type of interfacing soil and composited for later chemical and physical analysis. A completed soil blank column may be seen in Figure 4.

Introduction of dredged material to lysimeter columns

120. Prior to filling the columns, the top 5 cm (2 in.) of dredged material was scraped off and discarded, eliminating any material that might have come into lengthy contact with air during sampling, shipping, or storing. Approximately 2.5 cm (1 in.) of the dredged material around the outer circumference of each sample bucket was also discarded.

121. Using acid-washed nylon scoops and spatulas, the dredged material was immediately transferred from the sample buckets to the lysimeter columns. After a layer of approximately 1.25 cm (1/2 in.) of dredged material had been placed in the columns, air pockets were immediately smoothed out with nylon utensils, until 30 cm (1 ft) of dredged material had been placed on top of the interfacing soil in each lysimeter column. The volume and weight of dredged material added to each column were recorded. The quantity of a specified soil and dredged material added to each column is indicated in Table 10. A completed lysimeter column with dredged material and interfacing soil may be seen in Figure 5.

Removal of interfacing soil
and dredged material from
lysimeter columns

122. Because leachates were collected under a nitrogen gas atmosphere, sulfide was driven from the system in the form of hydrogen sulfide, making the subsequent calculation of leachate redox potential difficult. To estimate the redox potential of both the dredged material and interfacing soils, samples of each were removed from the lysimeter columns under anoxic conditions at the conclusion of both Phase I and Phase II of the experimental program, and the interstitial waters of both were extracted and analyzed.

123. To preserve redox conditions of the dredged material and the interfacing soils, the materials were removed sequentially from the lysimeter columns under anaerobic conditions. Each column and necessary support equipment (two sets of nylon spoons and spatulas and two hermetically sealing 19-l (5-gal) buckets, one each for the dredged material and interfacing soil and a waste bucket) were enclosed in a glove bag purged of air with nitrogen gas and kept under a nitrogen atmosphere throughout the process (Figure 6).

124. After the nitrogen atmosphere in the glove bag had been firmly established, the upper layer of oxidized dredged material was removed and discarded in the waste bucket. The dredged material inside the glove bag was scooped out with one set of nylon spoons and spatulas and placed in one of the hermetically sealing buckets, until the bucket was filled or the interface between the dredged material and soil was reached. At this point, the bucket was sealed. Any remaining dredged material was discarded into the waste bucket. In the same manner, the soil was removed with the second set of nylon utensils. After the bucket containing the soil was sealed, the glove bag was opened; the polypropylene beads were removed from the

lysimeter column and placed in glass containers which had been cleaned with petroleum ether. The beads were later extracted with petroleum ether and the extractant analyzed for chlorinated pesticides and PCB's.

125. Column 6 was somewhat different; to examine the internal migration of constituents, two samples were taken of both the dredged material and the soil and kept separate as the top and bottom dredged material and top and bottom interfacing soils.

126. The samples of dredged material and soils were sent to the University of Southern California, Department of Environmental Engineering. Interstitial waters were extracted under a nitrogen atmosphere using a Carter Press. Due to the small sample size, they were analyzed only for trace metals and total sulfides.

127. After each column was completely free of dredged material, interfacing soils, and polypropylene beads, the cleaning procedures mentioned above were repeated and the column prepared for the next round of experimentation.

Lysimeter column operations

128. The laboratory portion of the study project was divided into two phases. In Phase I, eight dredged material and interfacing soil permutations were subjected to simulated rainfall conditions (alternating wet-dry cycles) by adding ultrapure (18 megohm) distilled water to the lysimeter columns; two soil-only columns served as analytical "blanks." The experiment was designed to generate 2 l of leachate per month. However, due to the extremely low permeability of some types of dredged material, less than 2 l/month of leachate was sometimes collected. Moreover, in the short dry period of 10 days allotted, the columns of dredged material did not dry out but remained saturated.

129. Except for Columns 5 and 9, the lysimeter columns were operated for six months in Phase I. Columns 5 and 9 were allowed to dry for an additional three months; a final leachate sample taken at the end of nine months showed Columns 5 and 9 to still be almost completely saturated except for the upper several centimeters.

130. Phase II of the experiment employed six columns. Dredged material from the Houston, Texas, area was placed in five columns with Perkins loam interfacing soil and in one column with Lake Arrowhead sandy loam interfacing soil. The objective of Phase II was to assess the relative variance in leachate quality caused by different leaching fluids. Phase II of the lysimeter column experiment was operated for three months.

131. The permutations of dredged material, interfacing soils, and leaching fluids investigated in both Phase I and Phase II are presented in Tables 11 and 12. The characteristics of the leaching fluids are discussed more fully in the "Results and Discussion" section of this report.

132. In Phase I and Phase II of the experiment, various leaching fluids were added at the top of the lysimeter columns; the leachate samples were collected at the bottom of the column after passing through dredged material and/or interfacing soil. Dredged material interstitial pore water samples were taken from the sides of the columns through polypropylene samplers by vacuum pump evacuation (Figure 2).

133. As mentioned above, the expected 2 ℓ /month of leachate was not always generated. In the few instances where lysimeter column percolation rates exceeded the desired 2 ℓ /month rate, flow control and subsequent saturation of the dredged material and soil were accomplished by raising the leachate collection bottles (Figure 3). This simple operation allowed approximately equal fluid contact times in all lysimeter columns.

134. Samples of leachate and interstitial water were drawn from each column every 30 days. As previously discussed, the design of the leachate collection system of the columns provided preservation of anaerobic conditions and continuous refrigeration of leachate samples.

135. Volume levels in the collection bottles were monitored daily; the connecting hoses were drained into the bottles at this time. At the end of the 30-day sampling period, each collection bottle was removed, capped, and replaced with a new, acid-washed bottle. At this time, the interstitial water samples were taken. A vacuum was applied to the interstitial sampling ports, and a sample of up to 500 ml was taken. Because of the low permeabilities of several types of dredged material, this 500-ml optimum was not always attained.

Analytical procedures

136. The chemical and physical analyses of dredged material and interfacing soils were performed by the University of Southern California, Department of Environmental Engineering and SCS Engineers. The analyses performed by each laboratory are delineated in Table 13; leachate and interstitial pore water samples were also analyzed by Weck Laboratories, Inc., Industry, California (Table 14).

137. Refrigerated centrifugation at 20,000 rpm for 20 min at 20°C separated the leachate samples into soluble and total fractions. After partitioning, each sample was divided into three parts for analysis by each of the three laboratories. Not all analyses were performed on each fraction, since some of the constituents exist only in the soluble or total fraction. The analyses performed on each fraction are listed in Table 15.

138. SCS Engineers performed conductivity and pH tests immediately upon receiving the samples; remaining

samples were frozen until other analyses could be performed. The leachate samples (both soluble and total) were preserved with ultrapure nitric acid and refrigerated at 2°C to 4°C until analyzed for trace metals. Only the soluble fractions of the interstitial pore water samples were analyzed, since the filter candle material used in the construction of the samplers contained pore size openings approximately 0.45 μ which filtered out the particulate fraction, leaving only the soluble fraction in the interstitial waters.

139. The physical and chemical analytical procedures used in this project are summarized in Appendix A; any deviation or modification is noted.

Characterization of Experimental Materials

140. The soil and dredged material used in the column leaching study were physically and chemically characterized. Physical properties are presented in Table 16. Textures ranged from sandy loam to silty clay, with corresponding decreases in permeability. The bulk densities reported are those estimated for the packed columns.

141. The chemical properties of the soil and dredged material are given in Table 17. The pH was measured in 0.01M CaCl_2 solution; the pH values are generally 0.5 less than in distilled water. The pH values very nearly represent those of the soil solution under field conditions and are independent of the initial amount of salt present in the soil or dredged material; the pH varied from strongly acidic to alkaline. Nitrate-N, ammonia-N, and chloride were determined from water extracts, metals were measured from nitric-hydrofluoric-perchloric acid digests (metal results are reported on a dry weight basis).

142. The dredged material contained large quantities of acid-soluble sulfides, which should greatly reduce the solubility and availability of heavy metals in the solution phase. The chloride content of the dredged material clearly indicates the freshwater or saltwater source from which the material was collected.

143. Perhaps, the higher concentrations of TOC, COD, oil and grease, chloride, and some heavy metals (Ni, Cu, Zn, Pb, and Cd) in the dredged material were due to industrial discharges into the harbor or channels; there are considerable variations in concentrations of the constituents among the types of dredged material.

144. Concentrations of the major cations and heavy metals in the interfacing soils and dredged material are shown in Table 18. The concentrations of exchangeable heavy metals varied greatly and constituted minor fractions of the total concentrations. The results indicate that iron was probably present as the solid phase oxides and hydroxides, which are not readily exchangeable.

145. Concentrations of chlorinated hydrocarbons (including PCB's) in soils and dredged material are given in Table 19. Some of the common insecticides, heptachlor, aldrin, endrin, and dieldrin, were all below detection limits. Concentrations of DDT and derivative compounds were present as traces, except for those in the dredged material from Mobile Bay. Except for the dredged material from Seattle, which was contaminated with PCB's, other soils and dredged material contained PCB's in concentrations less than 1 ppm. The results for individual soils and dredged material are discussed separately in the following sections.

Soil characterization

146. Lake Arrowhead sandy loam. The soil collected from the Lake Arrowhead, California, region is a

well-drained sandy loam relatively high in organic matter content accumulated from forest debris, which has resulted in acidic, low bulk density, high CEC, and water-repellent properties. The Lake Arrowhead soil is also low in total nitrogen, phosphorus, calcium, and magnesium, typical of acidic forest soils (Table 17). The potassium content of the soil, however, is somewhat high, probably due to the potash feldspar in the parent material. Concentrations of the heavy metals are within the range normally reported for soils.

147. Except for traces of DDT, no chlorinated hydrocarbons were detected.

148. Perkins loam. Perkins soil, collected near Hemet, California, is a moderately well-drained loam to silt loam with a pH varying from slightly acidic to neutral. Compared to Lake Arrowhead sandy loam, Perkins silt loam has lower CEC and lesser amounts of organic matter, COD, potassium, and oil and grease. Concentrations of the heavy metals are within the range typically reported for soils.

149. Again, traces of DDT were detected in the Perkins soil. Total PCB concentration was 16.6 ppb, primarily as PCB 1254. Insecticides, heptachlor, aldrin, endrin, and dieldrin, were not detected.

Dredged material characterization

150. Mobile Bay, Alabama. The dredged material from Mobile Bay, Alabama, was classified as a silty clay with low permeability (Table 16). The concentrations of TOC, COD, nitrogen, copper, cadmium, and calcium were the lowest among those for the types of dredged material used (Table 17). The material contained considerable amounts of iron, zinc, and acid-soluble sulfides. Since the Mobile Bay dredged material showed such a high concentration of acid-soluble sulfides, most of the heavy metals can be expected to be in the sulfide form.

151. DDT and its derivatives were all detected in the dredged material, with total DDT amounting to 507 ppb. PCB's were detected, but the concentration of 72 ppb is relatively low. Pesticides, heptachlor, aldrin, endrin, and dieldrin, were not detected in the dredged material.

152. Sayerville, New Jersey. The dredged material collected from Sayerville, New Jersey, is a silt loam with low permeability. Compared to the other types of dredged material, Sayerville had low CEC, ammonia-N, and manganese, but considerably higher total phosphorus, lead, and copper concentrations. The zinc, nitrogen, and cadmium concentrations were also high. However, the large quantities of acid-soluble sulfides in the dredged material should greatly reduce the solubility and availability of these heavy metals in the solution phase.

153. DDT was present in three isomers, totaling 99 ppb; PCB's, totaling up to 885 ppb, were detected primarily as PCB 1242 and 1254 (Table 19).

154. Grand Haven, Michigan. The Grand Haven, Michigan, dredged material is of freshwater origin; the chloride content is as low as 40 ppm. However, total concentrations of sodium, potassium, calcium, and magnesium were higher. The Grand Haven dredged material is a sandy clay loam with moderately low permeability. Concentrations of COD, TOC, total nitrogen, and nickel were greater than in the dredged material obtained from the other sites. The cadmium concentration of 23 ppm was also high. Only traces of chlorinated hydrocarbons were detected (Table 19).

155. Seattle, Washington. The dredged material from Seattle, Washington, is characterized by the highest concentrations of most of the constituents analyzed. Physically, it is a silt loam with 77 percent silt, low permeability, and high water-holding capacity. The concentrations of oil and grease, acid-soluble sulfides, sodium, potassium,

and magnesium were greater than those obtained from the other dredged materials; TOC and COD concentrations were also high. Heavy metal concentrations, particularly those of lead (50 ppm), cadmium (67 ppm), and zinc (445 ppm) are indicative of heavy industrial pollution.

156. Substantial quantities of PCB's (187 ppm) were observed in the Seattle dredged material, the result of a PCB spillage that occurred in 1974.

157. Houston, Texas. The Houston Ship Canal dredged material taken from the Clinton Disposal Area near Houston, Texas, is of brackish water origin, as indicated by the moderate chloride concentration of 4,480 ppm. The sodium, potassium, calcium, and magnesium concentrations are comparable to the other sites. The Houston dredged material is a silty clay of low permeability. Oil and grease and total nitrogen concentrations were the highest for any dredged material studied. The CEC was the second highest of any dredged material or interfacing soil studied. The CEC was the second highest of any dredged material or interfacing soil studied, and lead was high at 55.5 ppm.

158. DDT and its derivatives were all present in the dredged material in detectable quantities, while heptachlor, aldrin, endrin, and dieldrin were not. PCB's were detected in appreciable concentrations.

Characterization of Applied Leaching Solutions

159. To simulate upland disposal area environmental conditions, the chemical characteristics of the applied leaching solutions were varied. The leaching fluids utilized in the experiments were:

- Rainwater (Columns 1 to 10 and 12)
- Acid rainwater (Columns 11 and 16)

- Groundwater (Column 15)
- Fulvic acid solution (Column 14), and
- Municipal landfill leachate (Column 13).

Rainwater

160. To simulate rainwater, ultrapure (commercially deionized and distilled) 18 megohm water was used as the leaching fluid. This leaching fluid simulated the mobility of constituents between dredged material and interfacing soils without the complications of chelating and complexing agents. Because of atmospheric pollution, very little rainfall in the United States can be deemed pristine. However, the utilization of ultrapure distilled water was considered best for the experimental program.

Acid rainwater

161. Rainwater equilibrated with the atmosphere ($P_{CO_2} = 10^{-3.5}$ atm.) is slightly acidic, with a pH of 5.7. Recent studies have revealed much stronger acidity in rain, with pH values between 3 and 5. The depression of pH is primarily due to increasing amounts of sulfuric and nitric acids which are derived from sulfur dioxide and nitrogen oxides emitted into the atmosphere by combustion processes.

162. To simulate the acidic rainfall prevalent in the eastern United States, ultrapure distilled water was adjusted to a pH of 4.5 with sulfur dioxide gas. Thus, the pH levels were depressed, and simulation of the chemical state that may be expected in acid rainwater was provided.

163. The utilization of an acidic leaching solution allowed an assessment of the potential for increased mobilization of trace metals and other constituents in the dredged material solid/liquid interface.

Groundwater

164. To simulate groundwater intrusion into upland dredged material disposal areas, an artificial groundwater

solution was developed by adding alkalinity and hardness to ultrapure water. Alkalinity of 50 mg/l as calcium carbonate and hardness of 50 mg/l as calcium carbonate were added in the form of calcium chloride and sodium carbonate, respectively. These values fall into the ranges normally reported in the literature (53). Using carbon dioxide gas, the solution pH was adjusted to 6.0 prior to introduction to the lysimeter columns.

Fulvic acid

165. Fulvic acid ($C_{28}H_{16}(CO_2H)_8(OH)_7(CO)_3$, m.w. 195), was added to ultrapure distilled water for use as a leaching solution to simulate the effect of naturally occurring chelates on trace metal availability. The concentration of fulvic acid in solution was 75 ppm, which is close to the average value of 95 ppm reported by Schnitzer and Hansen (54).

Municipal leachate

166. One of the potentially productive uses of dredged material is for sanitary landfill liner material; leachate obtained from a municipal sanitary landfill was used as a leaching fluid to see if any increase in contaminant mass emission could be expected from dredged material. Of particular interest were the high organic and nitrogen contents of the municipal leachate. Organics are known to solubilize trace metals through chelation effects, and nitrogenous compounds in groundwater are a common and potentially serious public health problem. Table 20 lists the constituents in the municipal leachate used in the experiment. Most of the constituent concentrations fall within ranges reported for municipal leachates.

PART IV: RESULTS AND DISCUSSION

Introduction

167. The experimental results and subsequent interpretation and discussion of the results are included in this section. It is divided as follows:

- Results of lysimeter column operations
- Mechanisms for migration of constituents in dredged material and soils
- The migration of constituents in dredged material/leaching fluid systems
- The migration of constituents in interfacing soil/leaching fluid systems
- The effects of various leaching fluids on the migration of constituents in dredged material interfacing soil systems
- Summary of the migration of constituents in laboratory simulations of upland disposal of dredged material
- The potential impact of leachates from upland dredged material disposal sites on water quality, and
- The control of groundwater contamination from the disposal of dredged material in upland areas.

These six sections discuss the experimental results, including an assessment of the potential impact of upland disposal of dredged material on water quality. The final section discusses ways in which leachates from upland dredged material disposal areas can be controlled.

Results of Lysimeter Column Operations

168. The results of the lysimeter column experiments of Phase I are presented in Tables 21-59. Results for each individual constituent are tabulated separately; the data for each lysimeter column are presented for total leachate fraction, soluble leachate fraction, and

interstitial water. Figures 7-30 exhibit the same data graphically, plotted as concentration of constituents versus time. All plots are linear, except iron and manganese, where the concentrations of the constituents have been plotted on a semi-log cycle basis. Table 60 presents the results of the analyses of the interstitial water and leachates from Columns 5 and 9 after final pulse flow which followed the first six months of experimentation and three months of additional column drainage.

169. Tables 61 and 62 present the analyses of the polypropylene bead extracts for chlorinated pesticides and polychlorinated biphenyls. Results of the analyses of the interstitial pore waters of dredged material and interfacing soils removed from the columns at the conclusion of the experiment are presented in Table 63.

170. The analytical results of Phase II operations are presented in Tables 64-88 and graphically in Figures 31-52.

171. Because of the wide range of permeabilities of dredged material used in the experiment, flow rates of leaching fluids through the lysimeter columns varied significantly. Table 89 shows the average flow rates for each column. The flow rates for the columns containing dredged material from Mobile Bay and Houston were comparatively low. This could be interpreted to mean that the impact of leachates on groundwater, in certain cases, will be limited because of restricted flow.

172. However, in the study project, it was very difficult to obtain conclusive data on the leachates generated in the laboratory because there was not always a sufficient sample on which to perform all the analyses. When this occurred, priorities for analysis, based partly on the

volume of sample necessary for each type of analysis, were assigned as follows (in descending order):

- Trace metals
- Major ions
- TOC
- pH
- Conductivity
- Ammonia-nitrogen
- Cl
- PO_4 -P
- Total Kjeldahl nitrogen
- Nitrate-nitrogen
- Total phosphorus
- Chlorinated pesticides
- PCB's
- Oil and grease.

The lack of data for certain chemical constituents reflects these priorities.

173. Throughout the experiment, the dredged material in the lysimeter columns remained, for the most part, somewhat anaerobic. Each type of dredged material developed a thin (0.5 cm) aerobic crust at the top, usually a light brown color. Beneath this aerobic layer, the remainder of the dredged material was anaerobic and often in a highly reduced state, indicated by a light to dark black color. The exception was the Grand Haven dredged material in Columns 4, 5, and 9, which was greyish black with streaks of brown, indicating a diffusion of oxygen throughout. The soil blank columns remained aerated (brown) throughout their operation. The measured redox potential, indicating the actual oxidation state for each lysimeter column, may be seen in Figures 8 and 9; the measured oxidation states of the dredged material and interfacing soils are shown in Table 90.

174. The color of the leachates before extraction from the experimental setup was recorded. The range of color can be seen in Table 91, the only difference being intensity. The color, in most cases, may be attributed

to organic acids and/or iron precipitates; the darker the color, the more of these constituents present.

Migration of Constituents in Dredged Material/Leaching Fluid Systems

175. The transport of constituents to and from dredged material, which was discussed in a preceding section, is extremely complex. It is influenced and/or controlled by many factors, including dissolution, precipitation, diffusion, ion exchange, sorption, complexation, redox, and biological reactions, which may interact or occur simultaneously. Some of these factors may dominate for a short time, others may persist throughout the life of a site. It is impossible to derive a general model to explain the transport phenomena for all the constituents examined in this study; therefore, the interpretation of data will be based on each parameter.

pH

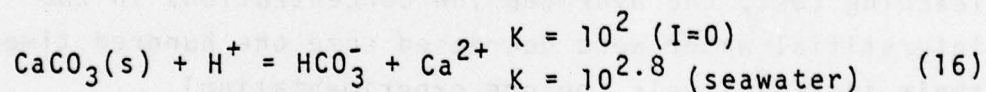
176. It was found that in one month pH values in the interstitial water were rapidly approaching 8 from original values of about 6.7 (Table 21 and Figure 7). After the leaching test, the hydrogen ion concentrations in the interstitial water were decreased some one hundred times their initial levels (before experimentation).

177. As discussed before, several mechanisms, such as organic decomposition, solubilization, and solid transformation, may be involved in regulating the pH level in the interstitial waters of dredged material. The decrease in hydrogen ion concentration may indicate that one or a combination of the following phenomena had occurred:

- Reduction of bioactivity after leaching fluid passed through the dredged material
- Dissolution of the pH buffering solids

- Reduction of inorganic solid transformation reaction, and
- Dilution of the interstitial water by leaching fluid.

178. Under the experimental conditions, the leaching fluid provided a continuous supply of dissolved oxygen to the surface of the dredged material; therefore, solid transformation will not be a significant factor for pH changes. However, this ongoing supply of oxygen into the system may tend to reduce anaerobic activities in the dredged material, thus decreasing hydrogen ion production. The dilution effect mentioned above, because it removes carbon dioxide, phosphoric acid, and hydrogen sulfide species from the interstitial water-dredged material system, may also decrease the hydrogen ion. However, it is suggested that the most important mechanism for regulating pH levels in this system is the dissolution/precipitation effect. In the natural sediment-seawater system, pH is usually buffered by silicate minerals or calcite (2, 81, 82). In this experiment, due to the continuous increase of calcium ion and carbonate concentration (to be discussed under alkalinity), the pH levels might be gradually buffered by calcite via the following dissolution reaction:



179. In most instances in this experiment, it was found that the soluble concentrations of Ca^{2+} and HCO_3^- were slightly oversaturated with respect to calcite; however, the K values calculated were quite close to the experimental K values.

Redox potential (Eh)

180. The Eh data of this experiment reveal that the dredged material from Grand Haven was maintained in a relatively oxidizing environment throughout the entire

experimental period; the Eh value averaged about 200 mV after the initial two months (Figure 8).

181. Compared to other types of dredged material, that from Sayerville remained in a relatively reducing state, while Eh values of the Seattle and Mobile samples were quite close to 0 mV. In general, the Eh values of the interstitial waters of the dredged material, with the exception of Sayerville, were oxidizing or slightly oxidizing during the initial two months. In all cases, at the end of those 60 days, the Eh values rose perceptibly, leveling out at the end of about 120 days. The Eh values of the interfacing soils remained oxidizing, for the most part, throughout the course of experimentation (Figure 9).

182. Dredged material with a relatively high organic content would be likely to have lower Eh values. However, Eh data from this experiment indicate that this does not always hold true. Among the types of dredged material studied, that from Grand Haven had the highest TOC content (4.77 percent) and the highest redox potential. This might be due to the difference in the oxidation rate of the organic matter in the dredged material, the flow rate of the applied solution, or the diffusion rate of oxygen into the dredged material.

183. The diffusion rate of oxygen in dredged material may be one of the most important factors for controlling the Eh level of interstitial water. From the particle-size distribution data, it can be seen that the Grand Haven dredged material has the highest sand content (50 percent) compared to the others (Table 16). The pore size of this dredged material appears to be larger; therefore, the dissolved oxygen can penetrate into the dredged material more easily. This explains why Eh values were always higher in Grand Haven interstitial water.

184. Researchers have shown that the penetration depth of oxygen in sediments is usually quite limited,

only a few centimeters (10, 52). The penetration of oxygen into dredged material might also be due to the flow of the leaching solutions. The flow rate in Grand Haven dredged material (an average of about 69 ml/day) was the highest of all the types of dredged material used in the experiment. The Sayerville dredged material had the lowest flow rate, about 26 ml/day and 19 ml/day in Columns 2 and 6, respectively, approximately one-third of the flow rate in the Grand Haven dredged material (Columns 4, 5, and 9). Because of the high flow rate in the Grand Haven lysimeter columns and the relatively low flow rate in the Sayerville columns, it is quite possible that the Grand Haven dredged material was more readily exposed to oxygen and, therefore, maintained a more oxidizing condition. The Sayerville material probably is inaccessible to oxygen diffusion and, therefore, maintained reducing characteristics throughout the entire experiment.

Total organic carbon (TOC)

185. The results of this study show that the soluble TOC levels in the interstitial water of dredged material were generally increased throughout the leaching test, from about 100 ppm to a range of 300 to 600 ppm (Table 22 and Figure 10). Column 1, where there was not enough sample to perform sufficient TOC analyses to demonstrate a trend, was the exception.

186. The release of TOC into solution has an important influence on the mobilization of constituents. Microbial activity in the interfacing soil may increase and consequently change the redox conditions of the resulting dredged material leachate, or complexation with trace metals may be enhanced, affecting the level of the trace metal concentration and consequent speciation.

187. Due to the complexity of the sediment-water system, the release mechanisms of TOC from dredged material

are not well known (83). Generally, chemical and/or biological processes are theorized (10, 83).

188. The soluble TOC level in the interstitial water of marine sediment is usually enriched. The concentration level may range from 40 to 300 ppm, about 40 to 300 times greater than the overlying waters (1, 10, 83, 84, 85, 86, 87, 88). During dredging, the high level of TOC is generally diluted by surrounding overlying water. A study by Blom et al. showed that after resedimentation of the dredged material, the TOC level can be increased (83). The increase was quite slow, but could gradually reach the original level.

189. In this study, it is quite clear that the transport trend of TOC is towards the original high concentration levels in the dredged material. Columns 3, 4, 5, and 9 show an initial lag time before TOC release (Figure 8); this is probably due to acclimation of microorganisms or dilution effect. The latter might become important, when the dissolution rate of organic species is low and the detention time of the leaching solution in pore space is short as at the beginning of the experiment.

190. It appears that levels of soluble TOC in interstitial waters do not correlate well with those in the bulk of the dredged material. The total organic carbon in the different types of dredged material is in the following descending order: Grand Haven (4.77 percent), Seattle (3.10 percent), Sayerville (2.82 percent), and Mobile (1.21 percent)(Table 17). The TOC levels in interstitial water, however, varied among the columns containing the same dredged material. Columns 4 and 5 (a replicated study of the Grand Haven dredged material) show a final level of 580 ppm, but Column 9 (the same dredged material but different interfacing soil) only released a level of about 300 ppm (Table 22 and Figure 10). This phenomenon also occurred in Columns 3 and 8. It has been speculated

that this is due to either the influence of the interfacial soil or the nonhomogeneous nature of the dredged material. However, this could imply that sediment organic carbon, viewed as a distinct, homogeneous component of sediments, may not be used as a reliable evaluative criterion.

Alkalinity

191. Throughout the experiment, the alkalinity levels in the interstitial waters of the dredged material gradually increased (Table 23 and Figure 11). The Sayerville dredged material caused the highest alkalinity increase, an increase of some 300 to 400 ppm (as calcium carbonate) over the initial study values. The interstitial water from the Grand Haven dredged material exhibited a slight increase in alkalinity values (about 200 ppm), while those in the interstitial waters of the Seattle dredged material in both Columns 3 and 8 were somewhat similar and rose from about 900 ppm to about 1200 ppm at the end of the experiment.

192. Alkalinity is an indicator of the acid-neutralizing capacity of the dredged material-leaching solution system. In interstitial waters, alkalinity can be caused by carbonate, borate, and ammonia species. Since the concentrations of borate and ammonia in interstitial waters are usually quite low ($4.5 \times 10^{-4}M$ and $7 \times 10^{-6}M$ to $1 \times 10^{-3}M$, respectively), the major part of alkalinity in the systems under discussion was probably due to carbonate species, especially bicarbonate. Table 24 lists the relative concentrations of alkalinity constituents in the final dredged material leachate (assuming borate concentrations are equal to $4.5 \times 10^{-4}M$). Because the interstitial pore sample was not sufficient, a comparison was impossible for the Mobile dredged material. The relationships between the constituents may be seen in Figure 11.

193. Carbon dioxide could not directly increase the alkalinity (mainly bicarbonate) which would result from

the dissolution of the carbonate solids (e.g., calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and other metallic carbonates or carbonate-silicate solids). The weathering of clay minerals requires longer contact time; this process is not important for the increase of alkalinity. As mentioned by Lu, the transformation of reduced metallic solids to oxidized metallic solids can also provide an increase of alkalinity (10). The importance of this transformation mechanism on the release of alkalinity is difficult to evaluate at this stage because phase transformation in the dredged material is largely unknown. However, it may become the dominant factor for the increase of the bicarbonate ion, if transformations occur rapidly. The relationship between the increased amount of bicarbonate and the amount of metals undergoing solid transformation may be expressed as:

1 M of metal transformed = 2 M of HCO_3^- released.

This means that when 100 mg of FeS(s) per kg of dry dredged material is transformed to FeOOH , approximately 350 ppm of HCO_3^- (as calcium carbonate) can be produced (assuming 50 percent moisture content in the sediment). Since the solution applied to the experiments under discussion is in an oxidizing condition, the transformation quantity of metal might become significant. In this experiment, therefore, the alkalinity must come from carbon dioxide production and metal transformation, but the alkalinity level was regulated by dissolution of carbonate solids in the dredged material. It is suggested that either calcite or dolomite could become the controlling solid for alkalinity, depending upon the pH and relative levels of Ca^{2+} and Mg^{2+} ions.

194. In comparing columns, it was found that the same dredged material would maintain virtually the same

level of alkalinity. The following order of concentration of alkalinity can be found at the final sampling point: Sayerville (1500 ppm), Seattle (1200 ppm), Grand Haven (550 ppm), the same order as the increased alkalinity previously discussed. In this experiment, there was no definite relation between alkalinity and dredged material characteristics, such as TOC or calcium.

Nitrogen compounds

195. Because it was difficult to obtain sufficient quantities of interstitial waters for analysis, data on nitrogen species were sketchy. It was found that the organic nitrogen levels in Columns 4 and 5 (Grand Haven) changed between the beginning and end of the experiment, from about 47 to 20 ppm to about 40 and 8.5 ppm, respectively (Table 25 and Figure 12). The values of organic nitrogen ranged from 47 to 5.5 ppm (Column 4).

196. In general, after the leaching tests, the concentration of ammonia-nitrogen and total Kjeldahl nitrogen (ammonia-nitrogen plus organic nitrogen) in the interstitial waters of the dredged material were found to be decreased, perhaps affected by both dilution and oxidation effects (Tables 26 and 27; Figures 13 and 14).

197. It has been suggested by Lu and Chen that the source of organic nitrogen in interstitial waters of sediment is mainly due to hydrolytic action on complex organic compounds and desorption by sediment particles. It was also found that the released amount of organic nitrogen was proportional to the total nitrogen content in the sediment and in inverse proportion to the redox potential of the sediment (16).

198. In this experiment, dredged material from Grand Haven had a slightly higher organic nitrogen content (1670 mg/kg) compared to the Sayerville sample (1250 mg/kg) (Table 17). However, the former had a lower organic nitrogen level in the interstitial water. Since

the Sayerville sample was in a more reduced state, it may be inferred that redox condition is more significant than total organic nitrogen content in controlling the organic nitrogen level in interstitial waters of dredged material.

199. Again, it has been suggested by Lu and Chen that ammonia-nitrogen sources in the interstitial waters of sediments are mainly from hydrolytic and biological reactions. A higher nitrogen content or lower redox state in the sediment could usually effect the release of higher ammonia-nitrogen levels into the interstitial waters (16). During the leaching test, the Sayerville sample, which had a lower nitrogen content than the Grand Haven dredged material sample, had the highest level of ammonia-nitrogen in the interstitial water (Table 26 and Figure 13). As with organic nitrogen, this may be dependent on the redox state of the dredged material. In addition, the relatively low flow rate of leaching solution in the Sayerville sample could also account for the higher level of ammonia-nitrogen due to a decreased dilution effect.

200. In this experiment, it was found that the Grand Haven dredged material had a higher redox state (in the range of +150 to +300 mV) than that of the Seattle sample (in the range of 0 to \pm 100 mV). However, the rate of decrease of ammonia-nitrogen was lower in the Seattle sample. This may be explained because:

- The nitrogen content in the dredged material might become more significant for regulating the soluble level of ammonia-nitrogen. Thus, the Grand Haven sample could replenish ammonia-nitrogen faster than the Seattle sample.
- The Grand Haven sample is a freshwater sediment; the Seattle sample is from a saline environment. During the leaching process by fresh water, the environmental change may be unfavorable to bacteria in the Seattle sample. The transformation rate of organic nitrogen to ammonia-nitrogen could be affected by the osmotic damage to the affected bacteria in the Seattle sediment, as suggested by Blom et al. (83).

201. Since the samples were insufficient, the migration data of nitrate and nitrite-nitrogen in the interstitial water of dredged material were incomplete (Table 28 and Figure 15). However, it is suggested that the changes of nitrate-nitrogen levels would closely follow those of ammonia and organic nitrogen. The soluble ammonia and organic nitrogen would eventually be converted to nitrate-nitrogen if a significant portion of the dredged material were to become aerobic. The nitrite-nitrogen should be in negligible levels, since nitrite is unstable in this tested environment.

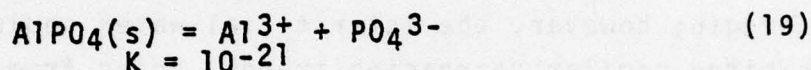
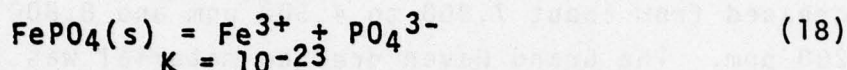
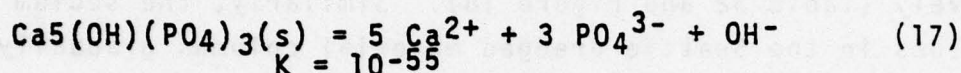
Phosphorus compounds

202. In general, the total soluble phosphorus and orthophosphate levels were quite low in the interstitial waters of the dredged material; the concentrations decreased as the leaching tests progressed. The concentrations of orthophosphate in the interstitial water were usually less than 0.01 ppm after a few months of leaching (Tables 29 and 30; Figures 16 and 17).

203. The transformation and movement of phosphorus in the sediment-water system have been discussed in the past by many researchers, e.g., Stumm and Morgan; Syers et al.; Lu and Chen; Blom et al.; and Spencer (16, 28, 29, 83, 89). As was previously mentioned, phosphorus in interstitial water may be controlled by solubilization, sorption, or biological reactions. In these experiments, it appears that the dissolution/precipitation effects may be the dominant factor.

204. Important phosphorus solids in dredged material include calcium, aluminum and iron phosphates and metal hydroxide-phosphates (such as $\text{Fe}(\text{OH})_x(\text{PO}_4)_{1-x/3}$, $\text{Al}(\text{OH})_x(\text{PO}_4)_{1-x/3}$), in addition to clay minerals and insoluble organic phosphorus. Among these, apatite ($\text{Ca}_5(\text{OH})(\text{PO}_4)_3$), strengite (FePO_4), and variscite (AlPO_4) are the possible

controlling solid(s) for regulating the phosphorus level in interstitial water because of the abundance of iron, aluminum and calcium in the dredged material and the low solubilities of these solids. This relationship may be seen as follows:



205. The formation of strengite needs a high redox potential, large phosphorus content and low pH. The calculations in Table 31 show the relative stability of apatite and variscite solids and the orthophosphate levels possible in the final leaching conditions of this experiment. From these calculations, it can be seen that the most stable phosphate solid in this experiment is probably the calcium phosphate solid (apatite). Although the calculations do not take into account the activity coefficient, it is quite clear that orthophosphate levels could be regulated down to the 1 ppb range by the calcium phosphate solid. This explains why, in this experiment, the orthophosphate levels in interstitial water were usually below the detection limit (< 0.01 ppm).

206. The concentrations of total phosphorus in the interstitial water of dredged material were also very low (Table 29 and Figure 16). As discussed by Lu and Chen, the polyphosphates and organically bound phosphorus in the interstitial and interfacial waters of sediments are usually negligible (16). Therefore, the total phosphorus levels might become quite close to the orthophosphate levels after a long period of leaching; this might also

account for low total phosphorus levels in the interstitial water of dredged material.

Sodium

207. In the lysimeter columns containing the Sayerville sample, sodium values gradually decreased from approximately 6,000 and 6,300 ppm to about 3,100 and 3,600 ppm, respectively (Table 32 and Figure 18). Similarly, the sodium values in the Seattle dredged material columns gradually decreased from about 7,800 to 4,500 ppm and 8,800 to 7,200 ppm. The Grand Haven dredged material was fresh water in origin; however, the interstitial water sodium values exhibited similar decreasing trends, going from 82 to 6 ppm, 70 to 42 ppm, and 79 to 31 ppm in Columns 4, 5, and 9.

208. Sodium in the interstitial water was found to decrease gradually throughout the experiment. After six months of leaching, the concentration of sodium in the interstitial water in most columns decreased to about half the original level. This may mainly be due to the dilution of the applied solution as well as the low dissolution rates of complex sodium solids.

209. Simple sodium solids such as oxide, sulfate, or halide are too soluble to exist naturally in sedimentary materials. Therefore, sodium solids in sediments are usually complex silicates; of these complex silicate solids, albite, Na-montmorillonite, natrolite, madeite, or hornblende may exist in recent marine sediments. The dissolution rate of these silicate solids is usually quite slow (28). If rate of dilution is greater than rate of dissolution, a decrease in sodium concentration may occur.

210. Theoretically, in order to dilute the sodium concentration to half the original level and assuming the dissolution rate is negligible, the volume of dilution water should be the same as the volume of interstitial water. However, in comparing the volume of the applied

solution and the interstitial water, it was found that the overall dilution factors were in the range of 14 to 40 percent. These relationships are as follows:

| Column Number | Pore volume of dredge material in Column (ml) | Overall applied solution (ml) | % Decrease of Na in interstitial water | Overall dilution factor (%) |
|---------------|---|-------------------------------|--|-----------------------------|
| 1 | 30,500 | 9,000 | -- | 23 |
| 2 | 25,100 | 8,500 | 49 | 25 |
| 3 | 33,100 | 9,500 | 43 | 22 |
| 4 | 27,500 | 13,500 | 32 | 33 |
| 5 | 27,500 | 18,000 | 40 | 40 |
| 6 | 25,100 | 7,500 | 42 | 23 |
| 8 | 33,100 | 5,605 | 18 | 14 |
| 9 | 27,500 | 18,500 | 60 | 40 |

211. Differences between the decreased percentage of sodium in interstitial water and the overall dilution factors led to the speculation that if dilution were the only mechanism for regulating sodium concentration in interstitial waters, a related effect probably occurred. It is possible that the mixing between the leaching solution and the interstitial water was not complete, i.e., there may have been a short circuit of the flow of the leaching solution in the pore space of the dredged material.

Potassium

212. The transport of potassium in the interstitial water of dredged material was similar to that of sodium. The dilution and low solubility rate of potassium solids probably played dominant roles in controlling the potassium levels. The results of the potassium analyses of the interstitial waters may be seen in Table 33 and Figure 19.

213. In general, the levels of potassium in the dredged material interstitial waters at the end of the experiment were approximately one-half those at the

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A STUDY OF LEACHATE FROM DREDGED MATERIAL IN UPLAND AREAS AND/O--ETC(U)

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beginning. The potassium values decreased in the Sayerville sample from 421 to 176 ppm and 432 to 197 ppm in Columns 2 and 6, respectively; the values of potassium in the interstitial waters of the Seattle sample decreased from 542 to 215 ppm and 590 to 293 ppm in Columns 3 and 8. While Grand Haven was a freshwater dredged material, similar decreasing tendencies were observed. In the third month of the experiment, however, potassium values in the interstitial waters of the Grand Haven material increased some four or five times that of the original concentration to 125, 165, and 110 ppm in Columns 4, 5, and 9, and then suddenly decreased again, as leaching time increased.

214. It is quite unusual to find, after about three months of experimentation, that potassium levels increased suddenly (in the interstitial waters of the Grand Haven sample). This sudden increase probably comes from the dissolution of a small quantity of simple potassium solids (which were enclosed by a thin coating of some other material) or perhaps because of potassium bearing colloidal particles.

Calcium

215. An examination of Figure 20 reveals that throughout the experiment, the calcium levels in the interstitial waters changed slowly, with a trend of increasing slightly at the beginning and decreasing at the end of the experiment. The levels of calcium at the end of six months were either close to or about 40 to 60 percent lower than the original concentration, depending upon the different dredged material.

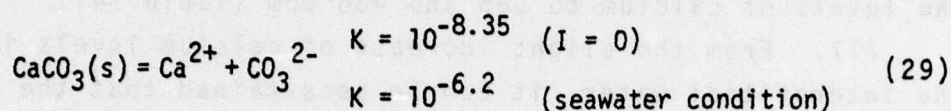
216. In experimental Columns 2 and 6, which contained the Sayerville sample, calcium values declined from 204 to 154 ppm and 211 to 114 ppm. In both columns, the levels of calcium seemed to decrease throughout the experiment. The calcium values for the Seattle dredged material ranged

from 161 to 60 ppm and 221 to 222 ppm in Columns 3 and 8, respectively. Column 8 had a peak value of 303 ppm of calcium at the end of the fourth month of column operations. In this project the calcium values in Columns 4, 5, and 9 (which contained Grand Haven dredged material) changed at the end of six months from 110 to 128 ppm, 110 to 120 ppm, and 121 to 94 ppm, respectively. The pulse flow through Columns 5 and 9 at the end of nine months sharply increased the levels of calcium to 565 and 436 ppm (Table 34).

217. From the slight increase of calcium levels in the interstitial water, it can be ascertained that the dilution effect was not a controlling factor in regulating calcium levels. The changes of levels can probably be attributed to the changes of the concentrations of some related anions which comprise the calcium solids, carbonates (CaCO_3 or $\text{CaMg}(\text{CO}_3)_2$), phosphates ($\text{Ca}_5(\text{OH})(\text{PO}_4)_3$, CaHPO_4 , etc.), and silicates (Ca-montmorillonite, wollastonite, idocrase, anorthite, etc.). Most probably either one or a combination of the ions (H^+ , CO_3^{2-} , PO_4^{3-} , SiO_3^{2-} , Al^{3+} , Mg^{2+} , etc.) from these solids affect calcium levels in dredged material-interstitial waters. Due to the abundance of carbonate in the dredged material pore water system and the kinetic constraint of complex calcium solids, it is quite possible that calcite might become the controlling solid for calcium. Then CO_3^{2-} levels (or alkalinity) should be directly correlated with calcium levels. Examination of the transport trends of calcium and alkalinity reveals an approximate correlation of this type. As previously discussed, in cases where there was not a distinct correlation, the calcium levels are probably affected by other ions.

218. In order to evaluate the possibility of calcite as the controlling solid for calcium migration, the following calculations were made:

The solubility products of calcite vary as ionic strength varies. Under these experimental conditions, if the controlling solid were calcite, the solubility product of calcite should be in the range of values from zero ionic strength to seawater conditions, as shown below:



Since the ionic strength of the interstitial water is unknown, accurate evaluation is impossible. However, from other studies, the following activity coefficients may be assumed:

$$\begin{array}{l} \text{Ca}^{2+}: \gamma_{\text{Ca}^{2+}} = 0.9 \quad (28) \\ \text{CO}_3^{2-}: \gamma_{\text{CO}_3^{2-}} = 0.09 - 0.2 \quad (1) \end{array}$$

219. The results of these calculations (made for the final leaching condition) demonstrate that calcium levels in interstitial water of dredged material would be quite close to the concentration regulated by calcite (Table 35).

Magnesium

220. The results of the analyses of magnesium are presented in Table 36 and Figure 21. In Column 1, which contained the Mobile dredged material, the values increased from 278 to 303 ppm (only two data points). The magnesium values in the Sayerville sample in Columns 2 and 6 changed from 400 to 416 ppm and from 445 to 444 ppm; each column exhibited a peak value after two months of leaching, 640 ppm for Column 2 and 614 ppm for Column 6. In the columns containing the Seattle sample, a slight increasing trend was

observed, with a peak value during the third month. The magnesium values ranged from 365 to 383 ppm with a peak value of 840 ppm in Column 8. Throughout the first six months of experimentation, the Grand Haven dredged material in Columns 4, 5, and 9 exhibited similar decreasing trends: the values decreased from 64 to 5.3 ppm, 62 to 5.2 ppm, and 62 to 3.4 ppm in Columns 4, 5, and 9, respectively. Results of the leaching after three additional months increased the magnesium levels to 77 ppm in Column 5 and 65 ppm in Column 9.

221. The magnesium levels in saltwater dredged material either showed no significant change or increased slightly in the initial leaching period and decreased in the long leaching period. In the freshwater dredged material, the concentrations of magnesium kept decreasing during the first six months of leaching, then an increasing trend again occurred.

222. In the interstitial waters, the levels of magnesium might also have been affected by the magnesium solids present in the dredged material and by the anions which complement the solid(s). The possible solids for magnesium in dredged material are hydroxides (e.g., $\text{Mg}(\text{OH})_2$), carbonates (e.g., MgCO_3 , $\text{MgCa}(\text{CO}_3)_2$, $3 \text{MgCO}_3 \cdot \text{Mg}(\text{OH}) \cdot 3\text{H}_2\text{O}$), or silicates (e.g., clinoenstatite, forsterite, vermiculite, etc.). Therefore, the H^+ , CO_3^{2-} , and SiO_3^{2-} ions could affect the magnesium levels in the solution.

223. It is speculated that, because of kinetic constraints, the complex magnesium solids (especially silicate solids) probably could not play important roles in regulating magnesium levels. The magnesium levels analyzed were probably from the solubilization of hydroxide and/or carbonate solids. An evaluation of these solids is shown in Table 37.

224. From these calculations, it can be seen that brucite is too soluble to control magnesium levels. Since

dolomite is extremely insoluble under these experimental conditions, it also is unlikely to account for the magnesium migration. Solubilities of both nesquehonite and hydro-magnesite are very close to the magnesium levels analyzed for saline dredged material. The low solubility of magnesium in freshwater dredged material might be caused by silicate solids. It is also possible that magnesium levels were regulated by the solid-solution effect of nesquehonite and dolomite, since the concentration levels of magnesium in freshwater dredged material were within the solubilities of two magnesium solids.

225. It is suggested that in short leaching periods, the magnesium in the saline dredged material was unaffected by dilution because of high magnesium levels and the relatively faster solubility rate of the solid. However, after long leaching periods, it was slightly affected by dilution because of the increase of the leaching fluid volume. Since magnesium in the freshwater dredged material was probably controlled by relatively insoluble solids and the slow dissolution rates of solids, dilution was very significant, as we can see from the migration curve (Figure 21).

Chloride

226. Throughout the course of the experiment, chloride levels were found to be slightly decreased in the Sayerville dredged material and slightly increased in the Seattle samples; the six-month changes were only 20 to 30 percent. However, in freshwater dredged material (Grand Haven), it was found that the chloride levels were decreased about 50 to 66 percent from the levels originally in the interstitial waters. The values of chloride in the dredged material interstitial waters in Columns 2 and 6 decreased from 10,000 to 8,200 ppm and 10,000 to 9,600 ppm, respectively (Table 38 and Figure 22). A decrease of 10,000 to 9,700 was observed in Column 3 which contained the Seattle sample, while an increase from 10,100 to 13,000 ppm was observed in

Column 8 which also contained the Seattle dredged material. The chloride values in the interstitial pore water of the Grand Haven dredged material decreased relatively constantly throughout the experiment, from 100 to 53 ppm, 100 to 48 ppm, and 140 to 29 ppm in Columns 4, 5, and 9.

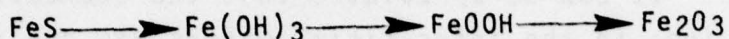
227. It can be speculated that the decrease of chloride ions in the interstitial waters was due primarily to the dilution effect. Because of the absence of simple chloride solids in the dredged material itself, it seems probable that the dissolution/precipitation effect does not control chloride concentrations in interstitial waters. The discrepancy between the changes in the chloride levels and the effects of dilution is most likely due to ion exchange.

Iron

228. In general, the results of this experiment indicate that the concentrations of soluble iron in the dredged material decreased between the beginning and end of the experiment, with a pulse value at the fourth sampling period (Table 39 and Figure 23). The Sayerville sample in Columns 2 and 6 produced iron concentrations that changed from 1.3 to 0.5 ppm and 1.0 to 0.5 ppm, respectively. The Seattle dredged material changes in interstitial iron concentrations decreased from 1.1 to 0.7 ppm and 0.8 ppm in Columns 3 and 8, respectively. Values of soluble iron in the Grand Haven samples (Columns 4, 5, and 9) increased from 0.4 ppm, 0.4 ppm, and 0.2 ppm to higher levels at the end of six months, while at the end of nine months the pulse flow through Columns 5 and 9 produced levels of 0.08 and 0.4 ppm, respectively.

229. Under oxidizing environments, iron is commonly present as hydroxide, oxide, and silicate solids (e.g., magnetite, hematite, goethite, limonite, and chamosite). Under reducing conditions, iron is usually present as sulfide solids (e.g., FeS , FeS_2 , Fe_3S_4) and Fe (II)

silicates (e.g., FeSiO_3) (3, 81, 90, 91, 92, 93, 94). A chemical transformation study by Lu demonstrated that when reduced sediments are kept under aerobic conditions, the iron solids on the surface of the sediment particles could be transformed as follows (10):



230. Since the formation of FeOOH takes months or years, the major iron solids remaining on the surface of the dredged material particles after the leaching experiments are probably a mixture of ferric hydroxide and goethite (FeOOH) (93, 94). Because of this transformation, it can be surmised that the available soluble free iron should decrease throughout the leaching test. The results of this experiment did show a decrease of soluble iron in the interstitial water during the initial three months of experimentation. When the leaching period increases, the soluble iron should decrease due to the formation of FeOOH . In this experiment, however, the continuing increase of TOC in the interstitial water probably forced greater quantities of soluble iron into the solution phase as mentioned in the discussions on TOC. This phenomenon probably accounts for the later increase of iron in the interstitial waters of the dredged material after about three months. In most cases, the soluble iron in the interstitial waters showed a decrease-increase-decrease-increase cycle, probably due to competition between various mobilization mechanisms: deposition (because more FeOOH was formed), complexation (because more soluble TOC was formed), and dilution due to the variation of flow rate.

231. After six months, the final soluble iron concentrations in the interstitial water samples of the Sayerville and Seattle dredged material were about 0.5 to 0.8 ppm and nil in the Grand Haven dredged material. This

could be attributed to the difference in the rate of solid transformation. The Grand Haven dredged material maintained a higher oxidation state throughout the experiment; consequently, the formation rate of $\text{Fe}(\text{OH})_3$ and FeOOH was faster in these samples than in the other dredged material. It has been clearly demonstrated by calculation that $\text{Fe}(\text{OH})_3$ can control the total soluble iron down to a level of 0.01 ppb (10). If soluble iron is controlled by FeOOH , the concentration of iron is several orders of magnitude lower. Therefore, in this experiment, it is possible that the soluble iron in the Grand Haven dredged material was controlled mainly by $\text{Fe}(\text{OH})_3$ and FeOOH , while in the other dredged material it was controlled mainly by FeS . As discussed by Lu, if the controlling solid of iron is iron sulfide, due to the complex formation of iron-carboxylic acids and iron-fulvic acid, the total soluble level can readily reach parts per million level, depending, of course, upon the organic concentrations (10). The levels of iron in this experiment were all in the range expected.

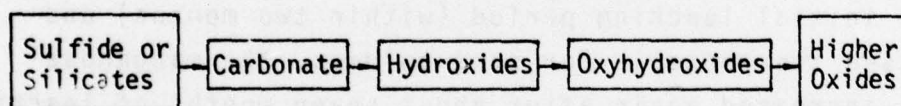
Manganese

232. In general, soluble manganese levels increased in the initial leaching period (within two months) and decreased thereafter. For some columns, the manganese levels increased again after about seven months of leaching (Table 40 and Figure 24).

233. Manganese values at the beginning and end of the experiment were 1.1 and 0.26 ppm for Column 2 and 2.9 and 0.25 ppm for Column 6; both columns contained the Sayerville dredged material. In Columns 3 and 8 (Seattle dredged material) the values of manganese went from 0.7 to 0.5 ppm and 11.8 to 3.1 ppm, respectively. In Columns 4, 5, and 9, which contained dredged material from Grand Haven, the manganese values at the beginning and end of the six-month study were 1.1 to 0.2 ppm, 1.5 to 1.25 ppm, and 0.5 to 0.6 ppm, respectively. The values of manganese in the

interstitial waters rose to 2.4 ppm in Column 5 and 1.36 ppm in Column 9 in samples collected at the end of nine months.

234. As previously discussed, the transport of manganese in the dredged material may be affected by solubility, adsorption, complexation, and dilution. The soluble concentration of manganese is controlled by the predominant solid(s) species in dredged material. The chemistry of manganese solids in dredged material is extremely complex. Mandal suggested that reducible manganese can exist in different forms, such as MnO , MnO_2 , Mn_2O_3 , and Mn_3O_4 (95). Ponnamperuma et al. found that more than 150 nonstoichiometric oxides of manganese ranging from $\text{MnO}_{1.2}$ to MnO_2 exist in nature (96). The chemistry and mineralogy of most of these oxides are largely unknown. In the experiment under discussion, the continuous leaching with aerobic water through the dredged material will probably change manganese solids in lower oxidation states to manganese solids in higher oxidation states. As has been demonstrated by Lu, when reduced sediments are oxidized, the transformation trends for manganese solids may occur in the following order (10):



235. Because of this transformation, the free concentration of manganese varies greatly in the solution phase. For example, if the predominant manganese solid in dredged material changed from MnS ($K_{sp} = 10^{-15.7}$) to MnCO_3 ($K_{sp} = 10^{-9.3}$) and then to Mn(OH)_x , MnOOH , and Mn_xO_y , assuming the original soluble sulfide was 5 ppm, the free Mn^{2+} concentration would increase from about 1 ppb to about 150 to 500 ppb depending upon the carbonate levels, then decrease again to the parts per billion or sub-parts per billion level,

depending upon the types of oxyhydroxides or oxides. This transport trend plays an important role in regulating the manganese levels in interstitial waters. Generally speaking, in this experiment, the data of manganese levels as a function of time support this statement.

236. In addition to solubilization, complexation might also affect the level and transport trend of manganese in the interstitial water of dredged material (47). The major soluble manganese species in the sediment-seawater system are MnCl^+ , MnCl_2° , Mn^{2+} , MnCl_3^- , and MnHCO_3^+ , which means either chloride or bicarbonate ions could become the important factor in regulating the manganese level and trend of transport through complexation. In this experiment, alkalinity data show that there was either a slight increase or no change. The chloride levels were either not changed or decreased. The importance of the two ligands can be seen in the calculations in Table 41. It can be ascertained from these calculations that in saline dredged material, chloride complexes are the most important soluble species for manganese and account for most of the soluble manganese analyzed. The slight decrease of the chloride ion in the interstitial water (as found in the Sayerville sample) could reduce the soluble manganese levels. However, this effect is negligible because the changes of chloride concentration in interstitial waters throughout the experiment were only about 20 percent. In contrast, as previously discussed, the change caused by solid transformation might be several orders of magnitude. The same argument apparently holds true for freshwater dredged material, the solubility of solids probably accounts for most of the difference; the soluble levels were mainly composed of bicarbonate complex and free manganese ion.

237. The effect of adsorption on manganese transport is difficult to evaluate; there is not sufficient information

on adsorption. However, it can be postulated that neither adsorption nor dilution were significant for the transport of manganese because of the strong influences of the other effects previously discussed.

Cadmium

238. The cadmium levels in the interstitial waters of the dredged material of this experiment may be seen in Table 42 and Figure 25. In general, after an initial low value, they reached a peak value during the second or third month of experimentation and, again, were lower thereafter. Some of the columns (3, 6, and 8) exhibited lesser peaks in the fifth or sixth month of the study. In the limited data of Column 1 (Mobile dredged material), the cadmium values went from 0.006 to 0.06 ppm. In Columns 2 and 6, which contained the Sayerville dredged material, the cadmium values decreased from 0.146 to 0.053 ppm and 0.123 to 0.060 ppm at the beginning and end of the experiment, respectively. In the interstitial waters of the Seattle sample the values went from 0.165 to 0.067 ppm in Column 3 and from 0.106 to 0.016 ppm in Column 8. The cadmium trends in the interstitial waters of the Grand Haven dredged material were quite similar in each of the columns. Data obtained at the end of nine months from Columns 5 and 9 exhibited only a slight increase. Between the beginning and end of the experiment, the cadmium values in the interstitial waters went from 0.0006 to 0.0002 ppm in Column 4, from 0.0006 ppm to almost nil in Column 5, and from 0.0009 ppm to 0.0002 ppm in Column 9.

239. It may be assumed that the soluble cadmium level in interstitial waters of the various types of dredged material during leaching tests will be controlled primarily by three mechanisms: solubility, adsorption, and complexation.

240. The solubility of the predominant solid(s) determines the transport of cadmium in interstitial waters. When soluble sulfides are present in the interstitial waters of dredged material, cadmium is usually precipitated out of the solution as cadmium sulfide (10, 97, 98, 99). If the solubility of cadmium is controlled by cadmium sulfide ($K_{sp} = 10^{-27}$), the free cadmium ion in solution is about 10 orders of magnitude lower than 1 ppb, depending, of course, upon the sulfide level in the interstitial water. Under aerobic conditions, the solid species of cadmium can be gradually transformed to hydroxide or carbonate forms (10, 99). Because of this transformation, the free cadmium ion concentration is greatly increased. In this experiment, the original types of dredged material were in reduced states; consequently, sulfide solids might possibly have controlled the solubility. However, during the leaching experiments, either $\text{Cd}(\text{OH})_2(\text{s})$ or $\text{CdCO}_3(\text{s})$ could be formed on the surfaces of the particles, increasing the free cadmium level by a factor of 1 million. Using the ion-ratio method,* it can be found that $\text{CdCO}_3(\text{s})$ was stable, due to a large amount of the carbonate ion present in the interstitial waters. If the free cadmium ion $[\text{Cd}_f]$ is controlled by $\text{CdCO}_3(\text{s})$, the level of $[\text{Cd}_f]$ can be solved as follows:

$$[\text{Cd}_f] = \frac{10^{-13.59}}{(\text{CO}_3^{2-})} = 0.007 - 0.12 \text{ ppb} \quad (35)$$

* Ion-ratio method: If a comparison is made between $\text{Cd}(\text{OH})_2$ and CdCO_3 solids, then the ion-ratio, (36)

$$R = \frac{\{\text{OH}^-\}^2}{[\text{CO}_3^{2-}]_f} = \gamma_{\text{CO}_3^{2-}} \frac{(K_{sp})\text{Cd}(\text{OH})_2}{(K_{sp})\text{CdCO}_3} = 0.2 \times \frac{10^{-13.80}}{10^{-13.59}} = 0.12$$

In the experiment, if the ratio of $\{\text{OH}^-\}^2$ to $[\text{CO}_3^{2-}]_f$ is smaller than 0.12, then CdCO_3 is more stable than $\text{Cd}(\text{OH})_2$.

241. In this experiment, except in the freshwater dredged material, the free cadmium ion alone clearly could not account for the analyzed levels. The complex formation might be far more important in accounting for the high levels of cadmium in the interstitial water. As mentioned by Lu, Hahne and Kroontje, Goldberg, Dyrssen et al., and Zirino and Yamamoto, the most important cadmium-inorganic complexes in natural water are cadmium-chloride and cadmium-hydroxide complexes (10, 85, 100, 101, 102, 103). Based on calculations of this experiment, only calcium-chloride complexes could be a significant species. The total concentration of cadmium-chloride complexes can be calculated from Cd_f and the cadmium-chloride formation constants: $\beta_1 = 10^{2.69}$, $\beta_2 = 10^{2.69}$, $\beta_3 = 10^{2.78}$, $\beta_4 = 10^{2.91}$, $\beta_5 = 10^{2.25}$ (24). The calculated and analytical results of the final conditions (after six months of experimentation) are as follows:

| Calculated and Experimental Cadmium Levels (all values in ppb) | | | | |
|--|--------|-----------------|-----------------|-----------------|
| Column | Cd_f | Cd-Cl Complexes | $Cd_f + CdCl_n$ | Analytical Data |
| 2 | 0.007 | 1.02 | 1.03 | 53 |
| 3 | 0.016 | 2.95 | 2.97 | 67 |
| 4 | 0.083 | 0.061 | 0.14 | < 0.2 |
| 5 | 0.12 | 0.076 | 0.20 | < 0.2 |
| 6 | 0.013 | 2.34 | 2.35 | 60 |
| 8 | 0.020 | 5.88 | 5.90 | 15 |
| 9 | 0.052 | 0.033 | 0.09 | < 0.2 |

242. From this table, it can be seen that the calculated results of cadmium in the interstitial waters of the freshwater dredged material are quite close to the analytical results. However, there is a considerable difference between the calculated and analytical results for the saline dredged material; the cadmium organic complexes probably

could be implicated. As suggested by Gardiner, the humic-cadmium complexes are the major cadmium-organic complexes in natural water (104). However, the nature and chemical composition of humic substances are not well understood. So, the possible cadmium level caused by humic substances is still unknown. Due to the high levels of TOC in the interstitial waters in this experiment, the cadmium-organic complexes could become the major reasons for high cadmium level. The freshwater dredged material had a higher dissolved oxygen content indicating that ferric hydroxide formation could become more important than cadmium-organic complex formation.

243. Although the level of cadmium in the interstitial water of dredged material could be explained by solid and complex formation, the trend of transport (cadmium level as a function of time) still can not be fully accounted for. Adsorption was probably involved; adsorption on colloidal surfaces due to coulombic-type forces has been suggested as primarily responsible for the migration of cadmium in soils (105). It is also possible that the major adsorbents in dredged material might be the colloids of clay minerals, humic substances, and hydrated oxides of iron and manganese. Both humic acid and clay-organic fractions display high selectivity, as well as high capacity for cadmium adsorption (60, 106). However, in this experiment, it is more likely that cadmium is related to the hydrated oxides of iron and manganese, because the transport patterns in the interstitial waters of dredged material were somewhat similar to those of iron and manganese.

Copper

244. The copper levels in the interstitial waters decreased significantly after about three months of experimentation. The final concentration of copper in the interstitial water (after six months) was less than 3 ppb.

(Originally it was 10 to 70 ppb). A pulse phenomenon occurred at the beginning with peaks at about two months after the start of the experiment (Table 43 and Figure 26).

245. The copper values in the Sayerville dredged material decreased throughout the course of the experiment, from 0.030 ppm in the beginning to 0.002 ppm at the end in Column 2, and from 0.038 to 0.001 ppm in Column 6. Similarly, the copper values in the Seattle sample decreased from 0.046 to 0.001 ppm and 0.065 to a level of nil in Columns 3 and 8, respectively. At the end of nine months, the additional analysis for copper in the interstitial waters of the Grand Haven dredged material followed the trends established through the first six months of the experiment: the values of copper decreased from 0.009 to 0.002 ppm in Column 4, from 0.018 ppm to nil in Column 5, and from 0.012 to 0.001 ppm in Column 9.

246. It was suggested by both Krauskopf and Garrels that in systems that are not acid and oxidizing, copper sulfides (e.g., chalcopyrite, chalcocite, and covellite) are the principal main solid species of copper (93, 107). When these solids are in contact with the zone of oxidation, carbonate hydroxide species may be formed; this transformation trend was also observed by Lu (10). The pulse phenomenon at the beginning of this test was probably due to the transformation of copper solids from CuS to $\text{Cu}_2\text{CO}_3(\text{OH})_2$, while the successive decrease of copper levels in interstitial water was probably due to adsorption and dilution effects.

247. Jenne and Krauskopf proposed that the hydrous oxides of iron and manganese provide the main control on the immobilization of copper in the soil/sediment-water system (49, 98). Therefore, the decrease of copper in this test was quite possibly due to the adsorption, coprecipitation, and occlusion of soluble copper with hydrous oxide solids. Another possibility is the dilution effect.

248. Since copper can be strongly bound with organic matter, clay minerals or hydrous oxides in sediment particles, the availability (water soluble plus exchangeable) of copper could be decreased due to the dilution from applied solution. Thus, the copper level in the interstitial water gradually decreased.

249. Although the trend of copper transport can be explained by the combination of solid transformation, adsorption, or dilution, the levels of copper in the interstitial waters of dredged material need additional explanation. Complexation is probably the only factor which can account for the copper levels in the experiment. Under the experimental conditions, both CuS(s) and malachite ($\text{Cu}_2\text{SO}_3(\text{OH})_2$) can control the free copper concentration down to below parts per billion levels (10, 29, 92). If the controlling solid for the free copper ion were an adsorbent, such as hydrous oxides, the free copper level could be as low as 10^{-13}M (75).

250. Only the formation of complexes raises the total soluble copper level to greater than 1 ppb. From calculations, Lu suggested that copper-carbonate complexes can increase the soluble copper level about 100 times higher than the free copper level (assuming $C_T = 10^{-2}\text{M}$) at a pH of 8 (10). Copper-borate complexes can raise these levels about 150 times higher (assuming $B_T = 5\text{ ppm}$) at the same pH value. If the solubility controlling solid were malachite, then the previous two major copper-inorganic complexes could increase the level as high as 100 ppb. However, if copper were controlled by adsorption or sulfide solid formation, the two copper-inorganic species noted above are not enough to account for the copper levels analyzed; copper-organic complexes should play an important role. Lindsay has estimated that for soil particles to regulate ionic copper from 10^{-13}M at a pH of 8 to $3 \times 10^{-8}\text{M}$ at a pH of 6,

the minimum K value for the copper-fulvic acid complex must be about 6×10^8 , assuming half of the TOC content was fulvic acid (92); this is indeed possible. Williams found that the formation constant of copper-organic complexes in seawater could be as high as 10^{18} (108). The formation constants of copper fulvic complexes discussed by Schnitzer, were $10^{3.3}$ and $10^{4.0}$ at pH=3, I=0.1, and pH=5, I=0.1, respectively (109). However, as pH increases to 8, the formation constant of copper-fulvic acid can be greatly increased. Since the chemical nature of dissolved organic matter is not clearly understood, a straightforward equilibrium calculation cannot be made.

Mercury

251. The analyses for mercury in the interstitial waters of dredged material exhibited a variety of trends (Table 44 and Figure 27). For the most part, they were in the parts per billion range and showed only slight fluctuations. Mercury levels in the Seattle sample are an example of this trend. In each column there was a maximum value in the first month followed by two slight peaks at the third and fifth sampling points. The initial peaks were 4.5 and 2.3 ppb in Columns 3 and 8, respectively. The secondary peaks were 1 and 1.1 ppb in Column 3 and 1 and 0.8 ppb in Column 8. Two peak values were reached in Column 6, (the Sayerville dredged material), at the first and third sampling point; however, the same sample produced the maximum value at the last sampling point in Column 2. The final value of mercury in the interstitial waters of the Sayerville sample was 0.5 ppb in Column 2 and 1.0 ppb in Column 6. Mercury levels at certain points in the Grand Haven sample show peak values higher than the other values during the experiment. A value of 4 ppb in Column 4 occurred at the third sampling point, while Columns 5 and 9 had peak values at the first sampling point and at the pulse flow at the end of

nine months (1.1 and 4 ppb in Column 5 and 3.1 and 3 ppb in Column 9).

252. At the pH conditions and redox potentials likely to occur in dredged material, Hg^0 and HgS solids, especially HgS , are the principal inorganic solids of mercury (110, 111). During the experiment under discussion, the transformation of HgS(s) to other inorganic solids such as oxide, chloride, or sulfate solids seems unlikely for the following reasons:

- The oxidation rate of HgS is very slow in sediments unless all other metallic sulfide solids are dissociated (29). Otherwise, through the sulfide competition effect (i.e., Hg^{2+} and $\text{MS} \longrightarrow \text{M}^{2+} + \text{HgS}$) the HgS will not be able to be converted to more soluble solids.
- The adsorption mechanism will decrease the soluble level if HgS can be transformed to other high solubility solids because mercury was found to be strongly adsorbed by manganese oxides or iron-oxides and also scavenged by organic matter (60).

253. If HgS(s) were the predominant solid in the dredged material throughout the experiment, the free mercuric ion could be regulated to very low levels because of its low solubility product (10^{-53}). As calculated by Lu; Goldberg; Dyrssen et al.; and Leckie and James, the major soluble inorganic mercury species are chloride and hydroxide complexes (10, 83, 84, 85, 94). In this experiment, the chloride complexes could raise the soluble mercury level in the interstitial waters of dredged material to about 7.6×10^{13} times that of the free Hg^{2+} concentration for the saline dredged material and about 1.6×10^8 times that of the free Hg^{2+} concentration for the freshwater dredged material. The HgOH^- complexes can increase the mercury level about 2.5×10^{10} times higher than that of the free Hg^{2+} in both types of dredged material. However, the solubility of mercury from HgS(s) is about $5 \times 10^{-24}\text{M}$, when soluble sulfide is negligible (112). If soluble sulfide is present, the Hg^{2+} concentration is even lower than $5 \times 10^{-24}\text{M}$. Thus, it is clear

that just mercuric chloride and mercuric hydroxide complexes alone cannot account for the mercury concentration in the dredged material-interstitial waters (about 0.2 to 1 ppb at the final sampling point). Therefore, the soluble mercury species in the interstitial water of dredged material should be mainly mercury-organic complexes. In seawater, mercury-amino acid complexes could become an important species for keeping mercury soluble; calculations in surface seawater demonstrated that mercury-amino acid complexes could raise the mercury level $10^{5.7}$ times higher than the free Hg^{2+} level (10). If it is assumed that the amino acid concentration is 20 times higher in interstitial waters than in surface seawater, the mercury-amino acid could potentially raise the mercury concentration about 10^{36} higher than the free Hg^{2+} concentration. In the experiment, the amino acid level is unknown; therefore, it is virtually impossible to ascertain the importance of mercury-amino acid complexes. However, the importance of these species cannot be overlooked. Besides mercury-amino acid complexes, the humic substances and proteins containing abundant sulfide groups also can form stable complexes with mercury (60, 111). These mercury-organic complexes might, in fact, account for almost all of the soluble mercury forms in the interstitial waters of dredged material.

254. The transport curves (concentration as a function of time) of mercury show that the mercury concentration was maintained at an almost constant level after about one month of leaching time. Some data points do show higher values of mercury in the interstitial water during the beginning of the experiment (usually before two months of leaching time). This implies that the original level of mercury was controlled by mercury sulfide and later by adsorption with hydrous iron and manganese oxides.

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Lead

255. There were two distinct trends for the levels of lead in the interstitial waters of dredged material, as may be seen in Table 45 and Figure 28. Columns containing dredged material from saline sources showed a slight increase. In all cases, the lead values in interstitial waters of the freshwater dredged material were less than 1 ppb after the first two months of experimentation. The levels of lead produced in Columns 5 and 9 by the pulse flow at the end of nine months also followed this trend. With this in mind, it may be noted that the values of lead increased in the Sayerville dredged material from 190 to 248 ppb in Column 2 and from 120 to 270 ppb in Column 6 throughout the experiment. Lead values in the interstitial pore water of the Seattle dredged material increased from 30 to 300 ppb and from 160 to 530 ppb in Columns 3 and 8, respectively. After initial peak values in the first monthly samples, the lead values in the dredged material interstitial water in the Grand Haven sample decreased to less than 1 ppb; for Columns 4, 5, and 9, between the beginning and end of the experiment, the lead values decreased from about 30 ppb to nil.

256. The behavior of lead, like many trace heavy metals, is strongly dependent upon environmental conditions. Under reducing conditions, lead forms a highly insoluble sulfide (97, 107, 111). Under normal oxidizing conditions, lead may become hydrolyzed and readily coprecipitated with hydrated oxides of more abundant elements. In addition, lead under aerobic conditions may be adsorbed by clay minerals, particularly on aluminum silicates. Under aerobic situations, some oxide, carbonate, or sulfate solids may also be formed, for example, PbO , $PbCO_3$, $Pb(OH)_2$, and $PbSO_4$ (28, 111, 113). There is also a great affinity for immobilization between lead and organic matter, but the most

stable solids of lead are usually found to be PbCO_3 in aerobic sediments (10, 60, 107, 110).

257. If the solubility of lead is controlled by $\text{PbCO}_3(\text{s})$, at the equilibrium condition, the free Pb^{2+} concentration can reach about 0.6 ppb (assuming $C_T = 10^{-2}\text{M}$) at a pH of 8. Pb-OH^- complexes (mainly Pb(OH)^+ , Pb(OH)_2^0 , Pb(OH)^- , and Pb(OH)_4^{2-}) can add an additional level of 1 ppb to the solution phase (10). The Pb-CO_3 and Pb-HCO_3^+ complexes together can raise the lead concentration in interstitial waters of dredged material to a level of about 200 to 250 ppb, chiefly in the form of PbCO_3^0 , $\text{Pb(CO}_3)_2^{2-}$, $\text{Pb(HCO}_3)_2^+$, and $\text{Pb(HCO}_3)_2^0$ (10). The lead-chlorine complexes are also important if the chloride level in the interstitial waters is high. In the experiment under discussion, lead-chloride complexes can increase to levels about 44 times higher than the free Pb^{2+} concentration for the saltwater dredged material, but only about 0.06 times the Pb^{2+} for the freshwater dredged material. Consequently, if $\text{PbCO}_3(\text{s})$ were the solubility limiting solid, the Pb-CO_3 complexes would constitute the majority of the soluble lead species in interstitial water. In this case, the lead level should be as high as 200 to 300 ppb at the final sampling point. At the end of this experiment, the soluble lead levels in the interstitial water of the saline dredged material were about 250 to 300 ppb, close to the levels previously discussed.

258. For the freshwater dredged material in most cases, the final concentration of lead in the interstitial waters was below 1 ppb, indicating that the adsorption mechanism was very important for controlling the soluble lead level. It is suggested that the main adsorbent was hydrous iron oxide, since the data clearly demonstrate that the conversion of soluble iron to hydrous iron-oxide solid was quite complete in the freshwater dredged material.

Zinc

259. In general, the analysis of zinc in interstitial waters exhibited either a slight decreasing or increasing trend. Columns 2, 6, and 9 had peak values in the fourth month of 0.8, 0.505, and 0.425 ppm, respectively (Table 46 and Figure 29). Between the beginning and end of the experiment, zinc values in the interstitial waters of Columns 2 and 6 (Sayerville dredged material) went from 0.04 to 0.06 ppm and 0.05 to 0.075 ppm, respectively. The zinc values in the interstitial waters of the Seattle dredged material increased from 0.08 to 0.25 ppm in Column 3 and from 0.06 to 0.12 ppm in Column 8. At the end of nine months zinc levels in the additional sample from Columns 5 and 9 were essentially the same as those at the end of six months. The zinc values in the interstitial water samples from the Grand Haven dredged material at the beginning and end of the experiment decreased from 0.04 to 0.02 ppm, from 0.05 to 0.02 ppm, and from 0.02 to 0.011 ppm in Columns 4, 5, and 9, respectively. Thus, it can be concluded that the analyses of zinc in the interstitial waters of dredged material show that two types of transport trends existed, first a decrease of zinc as a function of leaching time, second a pulse phenomenon with a high peak after about four months of leaching time. However, at the sampling point, the zinc level in interstitial water was in the range of 1 to 20 ppb. The soluble zinc level at the end of experimentation was higher in the freshwater than in the saline dredged material, the inverse of most of the other trace metals.

260. It is suggested that sphalerite (ZnS) is the most stable solid for zinc in reduced sediments (10, 93, 107). Upon oxidation of the reduced sediment, carbonate or silicate solids of zinc can be formed. Zinc also can exist in solid form in the soil/sediment by adsorption or

ion exchange (92, 114). The soluble inorganic species of zinc in natural waters are relatively simple at high pH values. At a pH of 8, the main inorganic species are zinc hydroxide complexes (Zn(OH)^+ , Zn(OH)_2^0 , Zn(OH)_3^- , and Zn(OH)_4^{2-}). Due to hydroxide complex formation, the concentration of zinc can be increased to about 10 times of the free Zn^{2+} concentration. Zinc-organic complex formation is also possible in the dredged material (54, 109, 115, 116). A formation constant in the range of $10^{1.9}$ to $10^{10.4}$ has been previously calculated (115). It can be seen that zinc levels can easily reach the parts per million ranges in dredged material interstitial waters.

261. In the experiment under discussion, it is difficult to evaluate the controlling solid(s) for zinc; $\text{ZnCO}_3(\text{s})$ is too soluble in this case. If just the zinc-hydroxide complexes are considered, the solubility of $\text{ZnCO}_3(\text{s})$ can reach as high as 700 to 800 ppb. It seems reasonable that $\text{ZnSiO}_3(\text{s})$ or zinc-clay minerals are the controlling solid species and can control the soluble zinc down to 1 and 0.005 ppb, respectively, if zinc-organic complexes were absent (10, 92). The control of soluble zinc in interstitial waters of dredged material might also come from the mixed solids (i.e., solid-solution). The reason for the pulse phenomenon in Columns 2, 6, and 9 is unknown, but was probably due to the sudden release by the short-lived ZnCO_3 solid or by zinc-organic complexes. If this is the case, the pulse would be decreased to normal levels by hydrated oxide solids or clay minerals.

Chlorinated hydrocarbons

262. In all, about 20 species of chlorinated hydrocarbons were studied: o,p'DDE; o,p'DDD; p,p'DDD; p,p'DDE; o,p'DDT; p,p'DDT; Arochlor 1242, 1254, and 1260; lindane; BHC; heptchlor; aldrin; heptachlor epoxide; kelthane; methoxychlor; chlordane; toxaphene; dieldrin; and endrin.

The results of the migration of these chlorinated hydrocarbons are listed in Tables 47 and 48. Because the sample was not sufficient, only a few data points are available: one month sampling points for Columns 1, 5, 8, and 9. The data show that the chlorinated hydrocarbons in the interstitial waters of dredged material were extremely low and below the detection limits of the technique utilized (Table 49).

263. These results prove that the chlorinated hydrocarbons were strongly bound with dredged material particles. As was discussed, adsorption (principally the formation of hydrogen bondings and van der Waals force between the chlorinated hydrocarbons and dredged material particles, e.g., clay minerals, iron and manganese-hydrated oxides and organic matter) was the dominant factor in the immobilization of chlorinated hydrocarbons in dredged material.

Migration of Constituents in Interfacing Soil/Leaching Fluid Systems

264. In this section, the discussion of the migration and attenuation of constituents in soils will be based on the interstitial water of the dredged material, the effluents from the control columns containing only the interfacing soil, and the effluent leachate from the dredged material/interfacing soil columns. The data on the interstitial water of the dredged material, as discussed in the last section, will also be considered as the data of influent to the interfacing soils.

General parameters

265. pH. The pH levels for the Lake Arrowhead and Perkins soils during the leaching tests were around 6.3 and 7.5, respectively, lower than in the influent leaching solutions where the pH was about 8. After leaching through the interfacing soils, the pH of the leaching fluid from

the interstitial water of the dredged material was generally decreased. The Lake Arrowhead and Perkins soils could decrease the pH of the leachate to about 6.8 to 7.1 and 7.6 to 7.8, respectively (Figure 7).

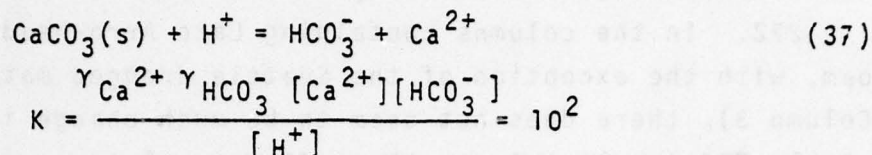
266. The pH levels in the leachates were higher than in the original soil solutions and lower than in the original leaching fluids from interstitial waters of dredged material, indicating that the hydrogen ion in the leaching fluids was affected by the interfacing soils. Compared to the original pH levels, the hydrogen ion concentration in the soil solutions was decreased by leaching fluids.

267. It is possible that this decrease of the hydrogen ion in the soil solution and increase of hydrogen ion in the leaching fluids were caused by the following:

- The soil solutions, with relatively high hydrogen ion concentrations, were diluted by dredged material leachates with relatively low hydrogen ion concentrations.
- Bioactivity in the soil solutions was reduced by dredged material leachates; therefore, the hydrogen ion production rate in the soil solution was reduced and could not maintain the original high levels of hydrogen ions.
- The alkalinity of the leaching fluids was decreased by calcite formation in the dredged material, thus increasing hydrogen ion levels in the final leaching fluids. However, the carbonic acid levels in original soil solutions were somewhat decreased.

It is suggested that the final pH levels in leachates would be gradually regulated by carbonate or silicate solids in the system. Due to the abundance of calcite and the relative slow dissolution rate of silicates, the controlling solid for pH might be calcite. If this is correct, the ion products of $[Ca^{2+}][HCO_3^-]$ should exhibit an increasing trend

and, thus, explain the decrease in $[H^+]$ in the leaching fluid, as in the following equation:



268. Generally, data of this experiment show increases of the ion products of $[\text{Ca}^{2+}][\text{HCO}_3^-]$. (For concentrations of Ca^{2+} and HCO_3^- , refer to the section on "Alkalinity." The calculations in Table 50 were made for final leaching conditions.)

269. As can be seen from Table 50, K_{out} 's were usually larger than K_{in} 's showing a trend of increasing pH in the leaching fluids. However, the increase of K_{out} 's (i.e., concentrations of $[\text{Ca}^{2+}][\text{HCO}_3^-]$) was mainly from the strong release of calcium and will be discussed later. The bicarbonate ion was actually decreased in the soil solution system, thereby causing the final hydrogen ion levels to be higher than the original leaching fluids, but lower than the original soil solution.

270. From the calculations in Table 50, it can also be seen that the equilibrium condition of calcite in a soil solution system was almost reached in Columns 4 and 5. The other columns are oversaturated with respect to the solubility of calcite. Therefore, for these columns, further precipitation of calcite can be expected, gradually decreasing the pH of the leachates.

271. TOC. Results of the control sets show that the organic matter could be leached from the interfacing soils significantly. The total TOC levels in soil leachates show an increasing trend during the first four to five months, as high as 800 and 200 ppm for the Lake Arrowhead and

Perkins soils, respectively (Table 22 and Figure 10). The total TOC level then decreased, probably because continuous flow decreased the availability of TOC from soils.

272. In the columns containing Lake Arrowhead sandy loam, with the exception of the Seattle dredged material (Column 3), there does not seem to be much change in the soluble TOC levels between the influent solutions (TOC in interstitial waters) and the effluent leachates. Leaching solution from Seattle dredged material, however, could solubilize a significant amount of TOC from the soil; the TOC levels were much higher than the control set. In general, after interaction of the dredged material leachates with the Lake Arrowhead soil, levels of TOC released from the soil were either unaffected or increased.

273. The Perkins loam columns, Columns 6, 8, and 9, also showed a release of TOC from the soil to the leaching solution. Since the TOC levels in effluents from these columns were higher than the control sets, there was obvious mobilization of organic species from the soils by leaching solutions from dredged material.

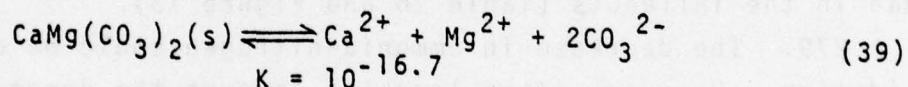
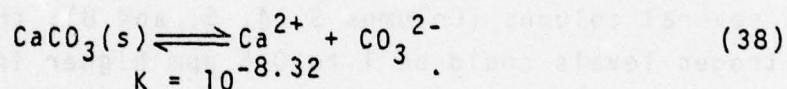
274. As mentioned before, the migration of TOC in these soil systems could result from solubilization, complexation, bioreaction, or sorption. These could either release or decrease TOC levels in leachates. However, due to the lack of knowledge of organic species and bioreactions in soil, accurate evaluation of the controlling mechanism is impossible.

275. Alkalinity. It was found that alkalinity levels in the leachates could be altered significantly by the interfacing soils. The levels of alkalinity in leachates from Columns 1 to 5, 8, and 9 were close to the levels in the control sets (Columns 7 and 10). If alkalinity in the influent solution (dredged material interstitial water) was

higher than in the leachates of the control set, the concentration decreased. If alkalinity in the influent solution was lower than in the leachates of the control set (only Column 9), the concentration increased (Table 23 and Figure 11).

276. As calculated, the alkalinity was mainly from carbonate species. The changes in alkalinity mean that the carbonate solids had been dissolved or precipitated. The carbonates of major elements, such as calcium and magnesium, and more specifically $\text{CaCO}_3(\text{s})$ and $\text{CaMg}(\text{CO}_3)_2(\text{s})$, were probably the primary solids involved. Although carbonate solids of trace metals could also affect alkalinity, they are relatively insignificant because of their low levels in solutions. The variation of these solids in the lysimeter columns in this experiment may be seen in Table 51.

277. The solubility products of the solids are also shown in the following equations:



From the solubility products and K values calculated in the table, it was found that either CaCO_3 or $\text{CaMg}(\text{CO}_3)_2$ was possibly the limiting solid in regulating the alkalinity. In most cases, of these two compounds, CaCO_3 is closer to the experimental results. Dolomite ($\text{CaMg}(\text{CO}_3)_2$) is usually formed by the substitution of magnesium for calcium in calcite solids (CaCO_3). The formation of dolomite is much slower than calcite. Thus, calcite is the most probable controlling solid in this experimental system. In most cases, the decrease of alkalinity could have been from the strong release

the soil. The calculated K values were also slightly higher than the solubility product of calcite in most cases. This was probably due to the release rate by ion exchange of calcium, which was faster than the precipitation rate of the calcite, indicating a slight oversaturation of calcite.

Nutrients

278. Nitrogen compounds. In the leachates of the control sets (Columns 7 and 10), the concentration levels of ammonia-nitrogen ($\text{NH}_3\text{-N}$) decreased to low levels (< 1 ppm) after long periods of leaching (about 4 months). The soil could contribute ammonia-nitrogen to the leachates only in the early leaching period (< 3 months). Ammonia-nitrogen in leaching fluids could be attenuated by soil after the initial period, probably through ion exchange. After several months of leaching (usually 2 to 3 months), the capacity of the soils to attenuate ammonia-nitrogen seemed to decrease in several columns (Columns 3, 4, 5, and 8); the ammonia-nitrogen levels could be 1 to 0.5 ppm higher in the effluents than in the influents (Table 26 and Figure 13).

279. The decrease in ammonia-nitrogen could be due to oxidation. However, after leaching through the dredged material, the redox potential of the leaching solution was greatly decreased (i.e., there were soluble sulfides in the interstitial waters), casting some doubt that ammonia-nitrogen oxidation can be the major mechanism of removal. The main pathway for removing ammonia-nitrogen is most likely ion exchange or adsorption. As reported by Preul and Schroepfer, physical adsorption on soil may become an important mechanism in the retardation of nitrogen travel, when the nitrogen is in the form of the ammonium ion (23). The subsequent increase of ammonia-nitrogen in the effluents of some column tests might be due to the saturation of adsorption sites or the conversion of organic-nitrogen to

ammonia-nitrogen (ammonification) as mentioned by Fairbridge (97).

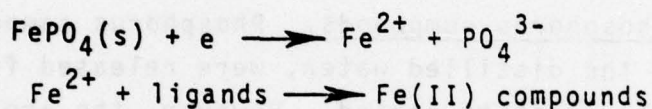
280. Total Kjeldahl nitrogen could be released from the soil (control columns) to about 20 ppm. After leaching through the dredged material and soils, the total Kjeldahl nitrogen in the effluents was significantly increased (Table 27 and Figure 14). In some cases, this increase was due to the increase of total Kjeldahl nitrogen in the influent. More often, however, the increase was derived from the soil. Bioconversion (which converted the insoluble complex organic matter into simpler soluble species) and/or simple leaching of the organic matter from the soils might be the most important mechanisms for this phenomenon.

281. Phosphorus compounds. Phosphorus compounds, when contacted by the distilled water, were released from the soils in the initial leaching period. However, the amount of total phosphorus and soluble orthophosphate in the leachates decreased to a very low level (0.01 ppm) after a long leaching period. After the dredged material leachates percolated through the soils, the soluble orthophosphate levels were still at a very low level; only a few data points showed relatively high values of total phosphorus (Table 29 and Figure 16).

282. As discussed before, the migration of phosphorus compounds in sediment/soil-water systems can be regulated by solubilization, sorption, and biological effects. Due to the slow reaction rates and small amount of phosphorus in soil organic matter, total decomposition of 1 unit of organic matter can only produce about 1/100 unit of phosphorus. Compared to other means, biologically-induced transport of phosphorus is usually negligible.

283. The initial release of phosphorus compounds could be derived from dissolution and desorption. As calculated in the previous section, solubility of apatite could control

the phosphorus to an extremely low level (about 0.00002 to 0.007 ppm in this experiment). Thus, the initial release of phosphorus compounds from soils could not possibly be from the dissolution of apatite. Aluminum phosphate (variscite) could not control the phosphorus levels because it is too soluble (solubility could reach levels of several hundred parts per million). If the initial release of phosphorus were caused by solubilization, the most likely solid responsible would be strengite (FePO_4). In this experiment, after the soils were flooded by water, the redox potentials of the soil solutions could be reduced and the phosphorus compounds released via the reduction of ferric phosphate to other ferrous compounds:



A quantitative calculation of the released phosphate due to the above reactions is impossible; there are many unknown ligands (especially organic ligands) in the soil solutions. However, it is suggested that the released phosphate could be scavenged by the high levels of calcium in the soil solutions and transformed from iron phosphate to calcium phosphate. This phenomenon could explain why the release of phosphate only occurred in the early stages of the experiment.

284. Desorption might account for the initial release of phosphorus compounds. However, this process is significant only when phosphorus compounds are preadsorbed by hydrated oxides of iron or manganese. Under a relatively reducing environment, these oxides could be transformed to lower oxidation states and higher solubility solids, and the preadsorbed phosphorus compounds released. The released

phosphorus compounds could also be scavenged by calcium, again reducing the phosphorus concentration.

285. Some data points show relatively high levels of total phosphorus in the leachates, perhaps due to the particulate forms of phosphorus percolated from the soils.

Major ions

286. Sodium. Leaching of the soils with distilled water (i.e., the control sets) showed a small amount of sodium released from the soils into the leachates, from about 10 and 150 ppm, from the Lake Arrowhead and Perkins soils, respectively (Table 32 and Figure 18).

287. Possible mechanisms for the release of sodium from soils by elution with water are dissolution and ion exchange. As mentioned by Griffin et al., the principal migration mechanism for sodium in soil is the cation exchange of sodium for calcium (11). However, since the initial sodium and calcium levels in the influent to the soil system were negligible, the exchange phenomenon should not be important. The dissolution of simple sodium chlorides from the original air-dry soils seems more plausible.

288. After the dredged material leachates contacted the interfacing soils, attenuation of sodium usually occurred; only in Column 9 (Grand Haven) was there elution of sodium.

289. Sodium is usually considered a mobile, relatively noninteracting cation in soil solution. However, either attenuation or elution occurred during leaching by dredged material leachates. In this experiment, the attenuation of sodium was more common, due to the high sodium levels originally in the leaching solution. Since simple sodium solids are very soluble, the attenuation of sodium could not be accomplished by simple solid formation. The nucleation rates of complex sodium solids are very slow (28), thus the attenuation of sodium due to complex sodium solid formation was also impossible. The most likely mechanism for the

attenuation in the soils might be cation exchange of sodium for calcium, as suggested by Griffin et al. (11).

290. The sodium elution phenomenon only occurred where the elution of sodium was actually due to the soil property itself; the sodium levels in the leachates of Column 9 were close to that in the control set (Column 10).

291. In the saline dredged material/interfacing soil columns, sodium levels increased as leaching time increased, indicating that the available exchangeable sites containing sodium were gradually reduced. The migration results of Column 3 are a good example of the relationship between the exchange capacity and sodium levels. When sodium levels in leaching fluids were lower than the saturation concentration developed by exchange equilibrium, a continuous exchange of sodium took place; otherwise, the phenomenon was reversed. For example, after three months of leaching, the sodium levels in the influents to the soils (about 4,400 ppm) increased to less than the equilibrium concentration (about 5,700 ppm) after elution took place.

292. Potassium. Data from the control sets (Columns 7 and 10) show that potassium could be leached out of soils by distilled water; after long periods of leaching, the soluble amount of potassium leached from the Lake Arrowhead sandy loam gradually decreased to about 20 ppm. The total amount of potassium leached from the same soil showed higher levels than the soluble potassium, but when leaching time increased, total levels were closer to soluble levels. In the Perkins loam, the leached potassium also decreased from high levels (higher than 185 ppm) to about 24 ppm (Table 33 and Figure 19). The release of potassium could be caused by dissolution and ion exchange. Because of their instability in solution, the simple potassium solids may only be present in an unsaturated soil; highly leached or saturated soils can not maintain simple potassium solids for a long period of

time. Both the Lake Arrowhead and Perkins soils were obtained from the unsaturated zone in the field. Therefore, the possibility of dissolution can not be neglected. The elution of potassium from soil may also be caused by ion exchange; this is probably less important because of the high purity of the leaching solution (distilled water) in this experiment. The solubilization of potassium chloride adsorbed on or present in organic matter and soil aggregates also cannot be ignored.

293. After applying the dredged material leaching solutions to the soils, the potassium levels in the leachates were increased significantly. In the initial stage (within about four months), there was a strong release from the soils of potassium to the leachates. Except for freshwater dredged material, the potassium levels were gradually reduced to those of the influent solutions after a long period of leaching. The potassium levels in the leachates from the freshwater dredged material/soil were supplied by the soils: the potassium was eluted from the soil at much higher levels than were observed in the influent leaching solution. In general, the attenuation of potassium by soils was not significant. Griffin et al. concluded that potassium could be supplied by soils, especially by montmorillonite, through calcium cation exchange (11). In this test, this phenomenon was not significant, probably due to the low content of high CEC clay minerals in the tested soils, as shown in the following tabulation:

| <u>Soil Type</u> | <u>CEC, meq/100g</u> |
|---------------------------|----------------------|
| Lake Arrowhead sandy loam | 35 |
| Perkins loam | 25 |
| Kaolinite | 3-15 |
| Illite | 10-40 |
| Montmorillonite | 100-150 |

294. Calcium. Calcium could be eluted from both control soils (Columns 7 and 10) by distilled water. The released trends of calcium from both soils were similar. Soluble calcium concentrations were released from relatively low levels to about 160 and 300 ppm for the Lake Arrowhead and Perkins soils, respectively; for total calcium concentrations, they were released in the range of 200 to 300 ppm. Compared to the control columns, the calcium levels released from soils by dredged material leaching solutions were noticeable; the soluble levels could be increased from initial low levels of 25 to 150 ppm to as high as 2,500 ppm, depending upon the combination of dredged material and soil type (Table 34 and Figure 20).

295. As discussed above, solubilization and ion exchange are the two most important mechanisms for regulating migration trends and levels of calcium. A quantitative evaluation of the solubilization effect is necessary to demonstrate which was the controlling mechanism: data show a positive relationship between migration trends of calcium and leaching time. If this were due to solubilization, calcium would become more soluble after leaching because of the changes in the calcium-controlling solid(s) or related ligands. Possible calcium solids in soils and their thermodynamic data are listed in Table 52 (see also Table 34). If the strong release of calcium were caused by these solids, then concentrations of HCO_3^- , Mg^{+2} , PO_4^{3-} , and H_4SiO_4 should also increase.

296. In this experiment, the pH of the soil solution increased after leaching. From calculation, it can be seen that there was not enough H^+ to dissolve such solids as $\text{CaMg}(\text{CO}_3)_2$ or to transform the solids of calcium-feldspar and calcium-montmorillonite to increase the rate of soluble

Ca^{2+} as leaching increased. The dissolution or transformation of these solids does not seem to account for the migration trends of Ca^{2+} .

297. The decrease in bicarbonate concentration indicated that calcite was precipitating instead of dissolving. $\text{Ca}_5\text{OH}(\text{PO}_4)_5$ is quite insoluble and could not account for the release of Ca^{2+} . Moreover, the dissolution and transformation rates of complex solids are usually quite slow. It is doubtful that calcium solids can regulate migration trends.

298. The more reasonable explanation for the calcium source is ion exchange. It has been reported that calcium ions can be replaced by other cations (11, 12). In this experiment, the ions which could contribute enough exchange capacity, through ionic balance, were sodium and possibly magnesium. Comparing the study soils, it was found that with the exception of the Seattle samples (Columns 3 and 8), the amount of calcium released would usually follow the CEC levels of the soils. In the test, it was also found that leachates from saline dredged material contained more calcium than leachates from freshwater dredged material. This, of course, was due to the sodium and magnesium levels: the saline dredged material leachates had much higher sodium and magnesium levels and thus the ability to exchange with calcium ions would be higher.

299. The concentration of calcium in solution might not be totally controlled by ion exchange. Because of the high calcium levels in the soil solutions, they would eventually exceed the solubilities of most of the calcium solids. Therefore, the levels of calcium might be regulated by precipitation. Among the common calcium solids, calcite, dolomite, and apatite were possible candidates

for this phenomenon. However, dolomite and apatite are unlikely to be soluble controlling solids since:

- The formation of dolomite would alter the formation of calcite. After calcite is formed, the Ca^{2+} in calcite may be replaced by Mg^{2+} and form dolomite; dolomite takes longer to form than calcite.
- The phosphate concentration in the soil solutions was extremely low. There were not enough phosphate ions available to precipitate the calcium ion.

300. Therefore, it is more likely that calcite is the controlling solid for regulating calcium levels:

- The carbonate ion in the soil solution was quite abundant
- The alkalinity levels were decreased as leaching time increased
- The analytical results for soluble calcium gradually approached the solubility of calcite (see Alkalinity).

301. Magnesium. The release of magnesium from the Lake Arrowhead sandy loam by distilled water was relatively small (about 3 ppm) in comparison to the release from the Perkins loam (about 160 ppm) (Table 36 and Figure 21). It is suggested that this difference in the release of magnesium between the two soils was from the difference in magnesium-solids. The magnesium-solids most likely responsible for this release include magnesium-hydroxides, carbonates, and silicates; their thermodynamic data and the calculated results of magnesium solubilities are shown in Tables 53 and 54.

302. Neither of the calculated results seem to be close to the analytical results. However, it is suggested that the release of magnesium in the Lake Arrowhead sandy loam was probably controlled by dolomite or other less soluble magnesium-silicate solids. In these solids, the kinetic constraint can slow down the release of magnesium. Since the magnesium levels in leachates kept increasing as a function of time in the Perkins loam, they were much

higher than the solubility of dolomite (0.007 ppm) The dissolution of the nesquehonite and/or desorption, or the solid solution effect caused by the mixture of dolomite and nesquehonite, were probably responsible for this release. Since there are little data on kinetic sorption and solid solution, it is difficult to evaluate these mechanisms.

303. Magnesium in the leaching solution from the dredged material was found to be significantly attenuated by interfacing soil (Column 9 was the exception). The migration trend was similar to that of sodium. In general, two mechanisms account for the removal of magnesium: precipitation and ion exchange. In this test, precipitation was not important because the magnesium levels in the leachates gradually increased. This shows that the formation of dolomite was not the controlling factor. Otherwise, the magnesium should maintain relatively constant values in the solution. The most likely controlling factor for the attenuation of magnesium was ion exchange. Magnesium might have exchanged the calcium ion from the clay minerals as did sodium.

304. The attenuation was not so dramatic in the test of freshwater dredged material/Lake Arrowhead sandy loam. Perhaps the low concentrations of magnesium in the influent to the soils did not have the capacity to replace Ca^{2+} . The elution of magnesium from the freshwater dredged material/Perkins loam (Column 9) was probably due to the high solubility of the magnesium solid(s) in the soil.

305. Chloride. Chloride was leached from both soils by distilled water (control columns, Columns 7 and 10). Perkins loam could release more chloride (about 600 ppm) than Lake Arrowhead sandy loam (in the range of 30 to 50 ppm in the soluble form); there was no relation between the released amount and the chloride content of the soil (Table 17, Table 38,

and Figure 22). Dissolution is probably the major mechanism for the increase of the soluble chloride levels in leachates from the control columns. The original soils were unsaturated, so the existence of simple chloride such as sodium and potassium chloride solids is possible. In fact, since the dissolution of simple solids of sodium and potassium coincided, the elution of chloride might come from the sodium and potassium chloride solids.

306. It was found that chloride from the dredged material leachates could be attenuated by soils, especially from the saline dredged material. The attenuation of chloride in the freshwater dredged material/interfacing soil systems was relatively small. Therefore, either attenuation or elution was possible, depending upon the relative levels of chloride in the leaching fluids and soil solutions of the control sets.

309. Because chloride is considered a mobile, non-interacting anion in soils, it is surprising to find this strong attenuation of chloride, especially at the beginning of the leaching test. This may be due to dilution which may have occurred because distilled water was used to pack the soils during their introduction to the column. Due to the absence of low solubility chloride solids in nature and the kinetic constraint of complex chloride solids, precipitation could not account for the attenuation. As previously discussed, ion exchange seemed the most likely mechanism for the control of migration in the soil-solution system.

Trace metals

308. Iron. Total iron concentrations in the leachates of the control sets (Columns 7 and 10) were found to be leached at significant levels and increased rapidly in four months. After four months, the leaching curves for total iron leveled off and remained relatively stable, about 70 ppm for the Lake Arrowhead sandy loam (Column 7) and 46 ppm

for the Perkins loam (Column 10) (Table 39 and Figure 23). The soluble iron levels in the leachates from the Lake Arrowhead soil also increased as leaching time increased, from 4 ppm at two months to about 12 ppm at seven months. However, the concentrations of soluble iron in leachates from Perkins loam were relatively unchanged, around 0.2 to 1.6 ppm throughout the entire leaching test.

309. Many important reactions can cause the release of iron from soil to leachates, e.g., dissolution, desorption, or complexation. In oxidized soils, such as the soils in this test, the major solid species of iron are usually oxides and hydrous oxides (28), among them, hematite (Fe_2O_3), goethite (FeOOH), lepidocrocite (FeOOH), and ferrosiferic hydroxide ($\text{Fe}_3(\text{OH})_8$) (94, 117). The transformation of these solids is highly pH and Eh dependent.

310. As suggested by Gotoh and Patrick, the increase in soluble iron in a flooded soil was encouraged by a decrease in redox potential and pH (94). The critical redox potential for iron reduction and the subsequent dissolution was between +300 and +100 mV at pH 6 and 7, respectively, and -100 mV at pH 8. The same authors also indicated that the redox potential in a waterlogged soil was largely governed by the Fe^{2+} - $\text{Fe}(\text{OH})_3$ system, in which the ferric oxyhydroxide was a mixture of goethite and amorphous material. In this test, the Eh values of Lake Arrowhead sandy loam decreased from about +570 to +300 mV in one month, then remained in the range of +200 to +300 mV. The pH value for this soil in the test was about 6.4. According to Gotoh and Patrick, the soluble iron could reach 15 to 1,500 ppm (94).

311. The soluble iron in the Lake Arrowhead sample in this test increased to 12 ppm in seven months. From the foregoing discussion, a continuously increasing trend would be expected after seven months. It is suggested that this

strong release was not just due to the reduction of oxyhydroxide of iron; the solubility of the mixture of goethite and ferric hydroxide is still quite low, as can be seen from the following calculations:

For Fe^{2+} - $\text{Fe}(\text{OH})_3$ system:

$$\text{Eh} = 1.057 + 0.059 \text{ p}[\text{Fe}^{2+}] - 0.177 \text{ pH} \quad (49)$$

$$\text{at Eh} = 270 \text{ mV, pH} = 6.4$$

$$[\text{Fe}^{2+}] = 10^{-5.86} \text{ M} = 0.08 \text{ ppm} \quad (50)$$

For Fe^{2+} - FeOOH system:

$$\text{Eh} = 0.429 - 0.029 \text{ p}[\text{Fe}^{2+}] - 0.118 \text{ pH} \quad (51)$$

$$\text{at Eh} = 270 \text{ mV, pH} = 6.4$$

$$[\text{Fe}^{2+}] = 10^{-20.2} \text{ M} = 3.5 \times 10^{-6} \text{ ppm} \quad (52)$$

The high soluble iron levels in the soil solution should come from iron complex formation. As calculated by Lu and Chen, possible complexes might be iron-citric acid, iron-humic complexes, or other iron-organic complexes (47). Therefore, the release of iron from the Lake Arrowhead sandy loam by leaching with distilled water appeared to be due primarily to solubilization and complexation. For the Perkins loam, the release of iron from the soil was relatively small, which may indicate that complexation was relatively unimportant in this soil. Since information on organics in soil is still lacking, an accurate calculation is impossible at the present.

312. After the dredged material leachates percolated through the soils, it was found that the migration trends of soluble iron in soil solutions were similar to those of the control sets. Soluble iron in the leachates of the dredged material/Lake Arrowhead sandy loam was found to leach out strongly from the Lake Arrowhead sandy loam, but the leachates of the dredged material/Perkins loam were

relatively close to the levels of the control set of Perkins loam. It also appears that the soluble iron levels in the leachates from the dredged material/Lake Arrowhead sandy loam were usually higher than the control set.

313. In comparing the Lake Arrowhead and Perkins soils, it can be seen that the Lake Arrowhead sandy loam released much more TOC into the soil solution than the Perkins loam (Figure 10). The CEC and TOC values of the soils are also higher in the Lake Arrowhead sandy loam than in the Perkins loam (Table 17), which is indicative of a high organic content soil. This might account for the strong release of soluble iron (e.g., from organic compounds) in the Lake Arrowhead sandy loam and the relatively small release in the Perkins loam.

314. Among the constituents studied, the difference in concentrations of soluble and total iron in the leachates was especially obvious. The concentration of total iron could be several hundred times higher than the soluble concentration of iron, indicating that a considerable quantity of leached iron was in the colloidal form. Because they have strong adsorptive characteristics, the high levels of iron colloid might have played an important role in the migration of other constituents. It is suggested that the high iron colloids in the leachates were caused mainly by physical scouring.

315. Manganese. After the soils were flooded with water, it was found that manganese could be released from the Lake Arrowhead sandy loam (Column 7, control set) to as high as 20 ppm and from the Perkins loam (Column 10, control set) to as high as 2 ppm. After the dredged material leachates percolated through the soil, it was found that the amount of soluble manganese leached out of the soils increased as leaching time increased, to as high as 120 ppm in the saline dredged material/Lake Arrowhead sandy loam test

and to as high as 20 ppm in the freshwater dredged material/Lake Arrowhead sandy loam test (Columns 3 and 9). With the exception of dredged material from Seattle, the manganese levels in the soil leachates of dredged material/Perkins loam, were close to those of the influent solutions, which in turn, were close to those in the leachates of the control set (Table 40 and Figure 24).

316. The migration of manganese in soil is usually affected by solubilization (which in turn is affected by pH and Eh values), microbial reduction (which is affected by different types of organic matter and environmental conditions), ion exchange, and complexation (10, 20, 96, 116, 118). As was suggested by Morgan, the solubilization effect on manganese for the natural system is very difficult to quantify (119). The main problems are:

- The large number and variety of manganese oxide species that may be involved
- The identification of the dominant solid species
- Complications caused by non-stoichiometry of the oxides
- Ignorance of the solid state of the complex oxides
- The uncertainty of the oxidation state of the metal before, during, and after reduction; and
- The limited pH range over which some equilibria may operate.

Although there are many difficulties in quantitatively evaluating manganese in soil-solution systems, many experiments and calculations show evidence of the presence of the following principal species (10, 96, 118):

- Mn^{2+} , MnHCO_3^+ , MnCl^+ , and MnCl_2^0 in the solution phase
- MnCO_3 , MnS and the hypothetical oxides corresponding to MnO_2 , Mn_2O_3 , $\text{Mn}(\text{OH})_2$, MnOOH , and Mn_3O_4 in the solid phase.

317. Thermodynamic calculations (Table 3) show that during the reduction of the soil solution system, $\text{MnO}_2(\text{s})$

can be transformed to MnOOH(s) when Eh is lower than +670 mV at pH 7, $\text{Mn}_3\text{O}_4\text{(s)}$ can be transformed to $\text{MnCO}_3\text{(s)}$ when Eh is less than +610 mV, at pH 7, and MnOOH(s) can also be transformed to $\text{MnCO}_3\text{(s)}$, as Eh decreases to +550 mV, at pH 7. If soluble sulfide is present in the system, MnOOH(s) can be transformed to MnS at +407 mV, at pH 7. In this experiment, Eh levels were much lower than the above-mentioned Eh values, so $\text{MnCO}_3\text{(s)}$ or MnS(s) could become the dominant solids. However, due to kinetic constraint, oxide or oxyhydroxide solids can still exist in the system and regulate the manganese migration.

318. To evaluate the importance of solubilization, some theoretical calculations are necessary (Table 55). By using these equations, the soluble free Mn^{2+} concentrations can be calculated. Based on the calculations, it can be seen in this experiment by substituting bicarbonate bisulfite, pH, and Eh values into the equations, $\text{Mn(OH)}_2\text{(s)}$, MnOOH(s) , $\text{MnO}_2\text{(s)}$, $\text{Mn}_2\text{O}_3\text{(s)}$, and $\text{Mn}_3\text{O}_4\text{(s)}$ would gradually lose their solubility regulating ability (the mixed redox potentials in the leachates were estimated in the range of ± 110 to ± 290 mV). The controlling solid or solids would gradually transform to MnCO_3 or MnS . The calculated results may be seen in Table 56. In these calculations, $[\text{HS}^-]$ was estimated from the final soil pore water data. These data may conflict with Eh data due to the nonequilibrium of the system, but the results are quite close to the results of the sets for freshwater dredged material/soil and saline dredged material/Perkins loam. However, the results of soluble Mn^{2+} in saline dredged material/Lake Arrowhead sandy loam (Columns 1 to 3) were significantly higher than the solubility controlled by MnS(s) or $\text{MnCO}_3\text{(s)}$.

319. As mentioned before, the difference between the calculated and analytical results might be due to complex formation. The inorganic complexes of manganese are chiefly chloride and bicarbonate complexes. In this experiment, the bicarbonate

levels decreased significantly and probably could not account for the strong release of manganese in the saline dredged material/Lake Arrowhead sandy loam columns.

320. Chloride levels in the leachates from these columns were also decreased after elution through the soils. However, the chloride levels in the leachates of the above-mentioned columns gradually recovered to their original concentrations. This means that the total manganese levels can be gradually increased to levels as high as six times the free manganese levels. Therefore, the increasing trends of chloride concentration in the leachates of Columns 1 to 3 might account for the increasing trends of manganese levels (the increasing trends for the two constituents were roughly similar), and the additional levels of manganese above the solubility of MnS(s) or $\text{MnCO}_3\text{(s)}$ might be mainly from the manganese-chloride complexes. Manganese-organic complexes could also account for the high levels of manganese. As mentioned by Geering et al. and Hodgson et al., the soluble manganese could be complexed with organic matter in the range of 28 to 99 percent, depending on the types of organics in the soil solutions (116, 120, 121). The possibility of manganese-organic complex formation cannot be ruled out. The columns containing dredged material and Lake Arrowhead sandy loam released relatively similar amounts of total and soluble forms of manganese. This indicates that the particulate forms of manganese in the leachates were small. However, the final leachates from columns containing Perkins loam showed that a greater quantity of particulate manganese could be leached by the leaching solutions. This phenomenon could come from the higher clay content (17.5 percent) of the Perkins loam.

321. Cadmium. Cadmium in the tested soils was roughly in the same concentration (1.5 mg/kg of dry soil), but cadmium

released from the Perkins loam (Column 10, control set) was much higher than that from the Lake Arrowhead sandy loam (Column 7) (Table 47 and Figure 25). As previously calculated, the free cadmium ion, inorganic cadmium complexes (mainly cadmium-chloride complexes), and cadmium-organic complexes can account for the cadmium levels. In this case, it seems that the cadmium-organic complex formation was not important in the release of cadmium; otherwise, the Lake Arrowhead sandy loam would have released more cadmium into the leachates than the Perkins loam and the cadmium levels in both leachates would have reached higher values (at least 10 ppb). When comparing the chloride concentration in the soils of the control columns, it can be seen that the release of cadmium was roughly proportional to the chloride levels, indicating that the released concentration of cadmium might be chiefly from the free cadmium ion and cadmium-chloride complexes; the cadmium in the control sets was thus most probably released by dissolution and inorganic complexation.

322. In comparing the soluble cadmium levels in dredged material and soil leachates, with the exception of the Seattle sample (Columns 3 and 8), cadmium was attenuated by soils during the leaching tests. In the columns containing the Seattle dredged material, cadmium levels were initially attenuated by the soils and remained relatively unchanged between influents (dredged material interstitial water) and effluents (soil leachates) after long periods of leaching.

323. The attenuation of cadmium by soil might come from precipitation, adsorption, or possibly decomplexation. As previously mentioned, precipitation is affected by solids transformations, the types and concentrations of ligands, the species of solids, and the solution conditions, such as ionic strength. In this experiment, it is speculated that

the most abundant cadmium solid in the soils might be the carbonate species. During the leaching test, a cadmium sulfide solid might be formed, due to the increase in free sulfide levels. This transformation trend was possibly one of the main mechanisms for the attenuation of cadmium. Table 57 shows the importance of solid phase transformations and the effects of soil solution changes on the reduction of the free cadmium ion (calculations were made on the final leaching conditions).

324. From this tabulation, it can be seen that if the solubility controlling solid changes from $\text{CdCO}_3(\text{s})$ to $\text{CdS}(\text{s})$ under equilibrium conditions, the free cadmium ion concentrations may decrease by about five orders of magnitude. Of course, in reality, the cadmium decrease would be modified due to kinetic constraint and the solid solution effect. However, from the calculations, it is quite clear that, in this experiment, cadmium could be attenuated by the soils through precipitation during the solid transformation reactions.

325. As suggested by Fuller, clay minerals, sesquioxides, and humic acids could become the major components involved in the adsorptive reaction for attenuating the cadmium in the soil (60). Therefore, in addition to precipitation, adsorption will play an important role for removing cadmium from the soil solution. However, quantitative information on cadmium adsorption by soils is usually lacking.

326. In this experiment, decomplexation could also control cadmium migration. The most important cadmium-inorganic complex is cadmium-chloride, which could account for an appreciable quantity of soluble cadmium. In this experiment, the chloride levels were significantly attenuated by the soils during the leaching tests; the decreasing cadmium level in the leachates could also be due to the

removal of chloride from the solution. In the tests of Columns 1, 2, 3, 6, and 8, the cadmium levels gradually increased again, and the chloride levels also increased significantly. This might mean that there was a relation between the migration trends of cadmium and chloride ion concentration.

327. From the above discussion, it is clear that the trend of cadmium migration can be explained by precipitation, adsorption, or decomplexation. However, it is suggested that the levels of cadmium analyzed would be controlled by complexation. As calculated, precipitation could regulate the free cadmium ion in the range of 5×10^{-10} to 7×10^{-4} ppm. Although the cadmium levels regulated by adsorption in this experiment are unknown, the free cadmium concentration should be down to the parts per billion levels (106). Therefore, the soluble levels of cadmium must come chiefly from the cadmium complexes. As calculated in the preceding section, cadmium-chloride complexes alone could not account for the levels analyzed; cadmium-organic complexes could also play important roles. Therefore, cadmium-organic complexes, in addition to cadmium-chloride complexes, should probably affect the migration levels and trends. The subsequent increase of cadmium concentration in the dredged material interstitial waters of Columns 1, 2, 3, 6, and 8, as mentioned, could also promote increased organic complexation. It seems that organic species released from the soil columns could not complex the large levels of cadmium. However, following the placement of dredged material on the interacting soils (except possibly for the Grand Haven dredged material columns) cadmium and TOC seemed to be released at higher levels. Since TOC levels showed increases comparable to the cadmium, it seems possible that organic complexation was important and resulted from interaction between the dredged material and soil.

328. Copper. The soluble copper released from the soils of the control set, Columns 7 and 10, was generally in the range of 1 to 5 ppb, very close to that in the dredged material leachates after a long period of leaching test. Therefore, the attenuation of copper by soils occurred only at the beginning of leaching, when the influent concentration of copper was at relatively high levels (higher than about 5 ppb). The Seattle dredged material/Lake Arrowhead sandy loam column (Column 3) was the only exception; it showed a slight release of copper after long-term leaching (Table 43 and Figure 26).

329. In soil-water systems, the migration of soluble copper has been found to be related to the following factors: pH, Eh, the soluble organic matter and carbonate levels in the soil solution, as well as the amount and type of clay, insoluble organic matter, phosphates, CEC, iron and manganese colloids, and microorganisms in the soil (50, 109, 122, 123, 124). As calculated by Lu, the major soluble species of copper in seawater are usually copper-borate, copper-carbonate, and copper-organic complexes (10). The concentrations of these complexes are pH dependent. The increase in pH in the soil solution (in this test, pH in the soil solution was increased about 0.5 and 0.3 units by the dredged material leachates for the Lake Arrowhead and Perkins soils, respectively) can decrease concentrations of the soluble copper-inorganic complexes slightly. Because of lack of information on copper-organic complexes, it is still difficult to find the importance of pH on the attenuation of copper by soil.

330. In this test, the effect of Eh on copper migration might be most important to the transformation of copper solids. The interacting dry soils were originally in an oxidizing environment (see the Eh data for the soils, Figure 9). The copper solids mainly existed as carbonates (such as

malachite and azurite) or silicates. After leaching, a relatively reducing state developed in the soils due to the soluble sulfide species: sulfide solids (e.g., covellite) might be formed which could reduce the soluble copper. The attenuation of copper could also come from redox changes in the soil solution.

331. Both soluble and insoluble organic matter have also been reported to be strongly related to the copper migration (122, 123, 124, 125). Either retention or release of copper is possible through the chelation of copper with soil or soluble phase organic matter. These complexation mechanisms have no doubt produced modifications in the migration patterns of copper.

332. Researchers have pointed out that the mobility of copper decreases with increased alkalinity, or carbonate content, of the soil solution (122, 126, 127, 128). This implies that the dissolution or precipitation of copper carbonate solid(s) could become one of the mechanisms in controlling the migration of copper in soil-water systems. In this test, the alkalinity in the leaching solutions decreased after they passed through the soils. The scavenging capacity of copper by carbonate solid(s) would also be decreased. Solubilization of the copper carbonate solid was not significant.

333. The amount and type of clay, as well as the amount and type of iron and manganese colloids, have been shown to provide the main control on the immobilization of copper in soils (49, 50, 60, 124). In this test, such colloids were quite abundant; the attenuation caused by adsorption cannot be overlooked. However, it is very hard to evaluate quantitatively.

334. The microbiological factors affecting the mobility of copper have been suggested (124). Bacterial activity should not greatly alter the copper concentration in this

test as chemical or physiochemical reactions had much greater ability to adjust the copper levels.

335. The migration of copper in the soil solution can be regulated by a combination of solubilization (in turn affected by pH and Eh), adsorption, and complexation. As previously described, if solubilization is caused by the copper-carbonate solid, copper-inorganic complexes alone can raise the copper level to 100 ppb. In this experimental situation, the controlling solid(s) might be either sulfide solids or adsorbents. If the controlling solid gradually became CuS(s) ($K_{sp} = 10^{-35}$), the free copper ion concentration would be in the range of 3×10^{-19} to 3×10^{-18} ppm. If the controlling solids were soil particles, the free copper ion concentration would be close to 6×10^{-7} ppm at pH 7 (92). In this experiment, copper-borate and copper-carbonate could only raise the soluble copper level about 100 to 200 times, not to the concentrations analyzed (10). Copper-organics could account for the total soluble levels of copper. However, as leaching time increased, the soluble copper gradually decreased. This phenomenon could occur because (1) more CuS(s) was formed, so the free copper ion concentration could be closer to the equilibrium condition set up by CuS(s) ; or (2) more iron colloids were leached out, so more copper ions were adsorbed.

336. In this experiment, a great many copper-particulates were leached out at the beginning of the leaching test. Just as for iron, this would come from physical scouring during dredged material emplacement in the columns; leaching then removed some of the small (colloidal-sized) suspended particulates from the soil solution.

337. Mercury. The migration trend of mercury in dredged material could also be controlled by the redox condition and adsorption; the levels of mercury would be controlled by complexation (mainly by organic complexes). As

suggested by Fuller, the movement and retention of mercury in soils and dredged material are controlled primarily by the same mechanisms (60).

338. There was not much difference in the levels of soluble mercury in the influent solutions and effluent leachates in this test (Table 44 and Figure 27). This would imply that the original mercury levels in the dredged material leachates were controlled by adsorption or the mercury sulfide solid: both the sulfide solid and adsorbent(s) of mercury are so efficient in regulating mercury concentrations that extremely low levels would be expected.

339. Leachable particulate mercury (mercury associated with clay minerals and insoluble organic matter or iron and manganese hydrous oxide solids) was several orders of magnitude higher than the soluble phase fraction; it is suggested that scouring was the principal reason for this release.

340. Lead. Leaching of the Lake Arrowhead sandy loam with distilled water caused the release of lead only at the beginning of the experiment. However, lead was observed in leachates from the Perkins soil control column (Column 10) in the 7 to 10 ppb range throughout the entire leaching period (Table 45 and Figure 28).

341. The soluble lead in the interstitial pore water from the saline dredged material was usually at high levels (see earlier section). After the leachates migrated through the soils, the lead levels were greatly reduced (close to the lead levels in the leachates from the control sets). As leaching time increased, the removal efficiency by soil gradually decreased. The soluble lead levels in the leaching solutions of the freshwater dredged material were relatively low; the lead levels in the leachates were easily attenuated by the interfacing soils.

342. In general, solubilization, adsorption, and complexation are the most important mechanisms for regulating the migration of lead in soils. As previously mentioned, solubilization is affected by pH, Eh, and solid species. In soil, lead can be easily precipitated as sulfide, hydroxide, and carbonate compounds, depending upon environmental conditions. It can be expected that solid lead species in flooded soil would gradually be transformed from carbonate to sulfide solids, due to the decrease in redox potential. In the equilibrium condition, without considering solid solution effect, if solid species of lead change from carbonate to sulfide, the free ion concentration of lead can be reduced about 8×10^4 to 4×10^7 times:

$$[\text{Pb}^{2+}]_{\text{PbCO}_3(\text{s})} = \frac{10^{-13.1}}{[\text{CO}_3^{2-}]} = 4.7 \times 10^{-10} - 4 \times 10^{-8} \text{ M} \quad (60)$$

$$[\text{Pb}^{2+}]_{\text{PbS}(\text{s})} = \frac{10^{-26.6}}{[\text{S}^{2-}]} = 1 \times 10^{-15} - 6 \times 10^{-15} \text{ M} \quad (61)$$

$$\frac{[\text{Pb}^{2+}]_{\text{PbCO}_3(\text{s})}}{[\text{Pb}^{2+}]_{\text{PbS}(\text{s})}} = 8 \times 10^4 - 4 \times 10^7 \quad (62)$$

343. In reality, complete solid transformation is impossible, but it can be seen that because of transformation, soluble lead could be greatly attenuated by soil. Attenuation of lead by soil due to an increase of pH (about 0.3 to 0.6 pH unit) in the soil solution was also possible; however, this attenuation (about 1 to 10 times) was relatively small in comparison to that of the solid phase transformations.

344. Lead is subject to surface adsorption, particularly on aluminum silicates and iron and manganese hydrous oxides, and has a great affinity for soil-bound organic matter (60). Again, quantitative information is unknown.

It is speculated that lead immobilization might be due principally to adsorption on clay minerals or the iron and manganese colloids. The transformation of carbonate solids to sulfide solids may also decrease lead levels. However, if solids transformations were important, the lead levels would be gradually decreased as time increased because more sulfide solids were formed. This is not true in this experiment. As a result, adsorption might become the only important factor for lead immobilization, and the decrease of attenuation capacity as time increased was due to a decrease in the effective adsorptive surface of the adsorbent.

345. Zinc. Zinc release patterns between the two interfacing soils were quite different. In general, Lake Arrowhead sandy loam could release about 3 to 10 times more soluble zinc (about 110 to 500 ppb) to the distilled water leaching fluid than would the Perkins loam. Because zinc was highly mobile in the Lake Arrowhead soil (Column 10), immobilization of zinc from the leaching solution was improbable (Table 46 and Figure 29). The leachable zinc in the Perkins loam (Column 7) was relatively low (about 10 to 40 ppb), but after the leaching solution was applied, immobilization was still not significant. The attenuations only occurred at unusually high concentrations (as high as 400 to 800 ppb) of zinc in the leaching solution.

346. As previously discussed, zinc could be controlled by silicates and some unknown zinc-soil solids. Although the levels of free zinc ion could be regulated by these solids to less than 1 ppb, three important effects took place in the soil solution that might greatly enhance the soluble zinc levels:

- Soluble TOC was usually released from the soil. Due to the high complexation ability of zinc and organic species, zinc was greatly mobilized.
- The adsorption capacity of zinc with clay minerals or iron and manganese colloids is relatively low

(on the order of $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+}$), not high enough to keep zinc levels down (80).

- The zinc sulfide solid is also relatively less stable than other sulfide solids (on the order of $\text{Hg} > \text{Cu} > \text{Pb} > \text{Cd} > \text{Ni} > \text{Zn}$). Through sulfide competition the zinc sulfide formation rate would be greatly reduced (10).

347. However, attenuation still took place where there were unusually high zinc levels in the influents to the soils. This indicates that zinc levels exceeded the equilibrium conditions developed by adsorption or solubilization.

348. Chlorinated hydrocarbons. Migration results of chlorinated pesticides and PCB's are given in Tables 47 and 48. In general, the individual species of chlorinated pesticides and PCB's were at very low levels, usually below the detection limits of the technique utilized. Table 47 is a summary of the concentrations of the chlorinated pesticides (about 20 species); Table 48 is a summary of the PCB species. Two conclusions can be made:

- The levels of chlorinated hydrocarbons were usually quite low, at less than 1 ppb; and
- There were no significant migration trends for chlorinated hydrocarbons.

349. As in the dredged material profiles, the chlorinated hydrocarbons were strongly bound with soil particles or had no input into the soil system. Therefore, chlorinated hydrocarbons were immobilized in the soil/leaching fluid systems.

350. At the end of the experiment, the polypropylene beads in the lysimeter columns were extracted and analyzed for chlorinated hydrocarbons (Tables 60 and 61). Of the 16 columns, only Columns 12, 14, and 16 showed some chlorinated pesticides and Columns 5, 12, 14, and 16 some PCB's. The quantities of chlorinated hydrocarbons adsorbed were extremely low if considered in the average concentrations in the total leachates; total chlorinated pesticides were in

the range of 0.001 to 0.02 ppb (tetrachloroethane extractant) and PCB's range from 0.09 to 1.06 ppb. This indicates that the chlorinated hydrocarbons bound by the polypropylene beads were usually negligible and further verifies the strong association observed between chlorinated hydrocarbons and the dredged material or soil particles.

Effects of Various Leaching Fluids on the
Migration of Constituents in Dredged Material
Interfacing Soil Systems

Introduction

351. To simulate varying environmental conditions that may be expected when dredged material is disposed in upland areas, different leaching fluids were introduced to lysimeter columns containing the same dredged material. The constituents of these leaching fluids are discussed in the "Characteristics of Experimental Materials" section of this report. The discussion which follows is based on the Phase II results of the experiment.

352. The trends for constituent migration in the dredged material/interfacing soil, as influenced by different kinds of leaching fluids selected to simulate various environmental conditions, are very difficult to evaluate. This is because of the short period of experimentation and, in certain cases, insufficient experimental results. The discussion of the effects of various leaching fluids on the migration of constituents will focus mainly on their levels and trends in the leachates. These will be compared with Phase I results.

pH

353. Results show that pH trends were quite similar in both the total fraction and interstitial water of the leachates in Columns 11 through 16. As can be seen in Table 64 and Figure 31, the trends were in the range of 7 to 8 with a majority close to 7.5. These results were very

similar to those for the soil blank columns (Columns 7 and 10) and the Phase I leaching tests, using the same interfacing soils. This phenomenon implies that pH levels in this leaching system could usually be kept within a very narrow range, i.e., the dredged material and interfacing soil could easily regulate hydrogen ion levels. Even in extreme cases, e.g., leaching by an acid rainfall solution with a pH of 4.5 (Columns 11 and 16), the leaching media still buffered the pH to normal levels.

TOC

354. Among the different leaching fluids, the migration trends for TOC in the leachates seemed to be quite irregular (Table 65 and Figure 32). Columns 12 (rainfall simulation) and 16 (acid rainfall simulation) showed a trend of decreasing TOC with levels down to about 100 ppm in the final sampling period of Phase II. However, other columns showed trends of increasing TOC with levels as high as 800 to 1,000 ppm after the same leaching period. Since there were no data on soluble TOC, it is impossible to evaluate whether the changes in the total TOC were due to soluble organic matter or organic particulates. The effects of high organic contents in the leaching fluids (Columns 13 and 14) are also difficult to evaluate accurately due to the lack of data on soluble TOC. However, the total TOC in the leachates of these two columns did reach higher levels in comparison to those for the column leached by distilled water (Column 12: rainfall simulation).

Alkalinity

355. The alkalinity results of Phase II may be seen in Table 66 and Figure 33. In Column 11, the alkalinity levels decreased greatly after interacting with Lake Arrowhead sandy loam; this decrease also occurred in Phase I of the experiment. In comparing Columns 12 to 16 (containing the same leaching media but different leaching fluids), the

alkalinity of the leachate in Column 16 (produced by the acid rainfall leaching fluid) was several times higher than the alkalinity in the leachate of other columns. The alkalinity in the leachates of the control set (Column 10) was similar to that of Column 16. Therefore, the large difference in alkalinity between Column 16 and Columns 12 to 15 must be due to the high hydrogen ion concentration in the original solution, which prevents the precipitation of calcium carbonate. If calcium levels are compared in the different columns of the Phase II study, the levels are much higher in Column 16 (the acid rainfall leaching fluid).

Nutrients

356. The results of the effects of leaching fluids on the migration of nutrients may be seen in Tables 67-72 and Figures 34-39. In general, there was no significant difference in concentrations of ammonia (Table 68 and Figure 37), nitrate (Table 70 and Figure 37) and orthophosphate (Table 72 and Figure 39) among the different column tests. However, slight differences were observed in the migration trends and levels of total Kjeldahl nitrogen (Table 69 and Figure 36) and total phosphorus (Table 71 and Figure 38).

357. Throughout Phase II of this study, total Kjeldahl nitrogen levels in the leachates of Columns 12 (rainfall simulation) and 13 (municipal leachate) increased, from 10 to 20 ppm to about 35 ppm. Levels of ammonia did not increase; therefore, organic nitrogen, in soluble or particulate form, is likely to be responsible for the rise in TKN. In contrast, the total Kjeldahl nitrogen levels in Columns 14 and 15 decreased, as the experiment progressed. There are limited data to aid in evaluating these trends. It is clear that the dredged material and/or interfacing soil can remove a considerable amount of total Kjeldahl

nitrogen from the leaching fluids. For example, the leaching fluid of Column 13 (municipal leachate) contained about 500 ppm of total Kjeldahl nitrogen; the effluent levels of this constituent were close to that of Column 12 (distilled water).

358. Total phosphorus also showed different patterns of migration in the different lysimeter columns, but phosphorus levels in the leachates for the different columns were similar (mostly in the range of 0.05 to 0.15 ppm). Because of limited data, it is difficult to explain the fate of this constituent in the different leaching environments. The only conclusion that is relatively clear is that the total phosphorus levels in all the Phase II lysimeter columns tended to reach the concentration of 0.1 ppm. Thus, in the long run, various leaching fluids might not have a significant effect on the migration of this constituent.

Major ions

359. The results of the Phase II experiment for the major ions are presented in Tables 73-77 and Figures 40-44. In general, the migration trends of major ions were quite similar to those of Phase I columns. Only sodium in the interstitial water and calcium in the leachates deviated.

360. The sodium levels in the interstitial water of the Houston dredged material were found to increase throughout the course of the experiment, a phenomenon for sodium migration unexplained by the chemical dissolution process (Table 73 and Figure 40). It is also unlikely that ion exchange was responsible for the strong release of sodium (about 1,000 ppm) and the relatively low levels of cations removed from the aqueous phase. This can be demonstrated as follows:

If exchanged sodium = 1,000 ppm =
 4.35×10^{-2} eq/l, then based on mass

law and electroneutrality, the summation of the removal of other cations should also equal 4.35×10^{-2} eq/L. This value is equal to 870 ppm of calcium, 529 ppm of magnesium, or 1,700 ppm of potassium.

In this experiment, the removal of these three major cations (calcium, magnesium, potassium) is much lower than the above-calculated values: the actual removal amount of calcium is 200 to 300 ppm; magnesium 10 to 70 ppm; and potassium levels are almost unchanged. Therefore, it is difficult to evaluate the increase of sodium in the interstitial water of the Houston dredged material during leaching. It might result from unusually high levels of simple sodium solids (such as sodium chloride) in the dredged material since chloride levels were also found to be greatly increased in some cases.

361. In comparing the columns utilizing different leaching fluids, it can be seen that the migration patterns of sodium were similar in both interstitial water and leachates of the different columns; there were minor differences in sodium levels among various leaching fluids. For example, in the final leachates from Houston dredged material/Perkins loam, soluble sodium levels in the leachates were in the range of 100 to 140 ppm, close to the variation of sodium levels (125 to 170 ppm) in the control set. Therefore, for all practical purposes, various leaching fluids have negligible effects on sodium levels in interstitial waters and leachates. This is probably due to the fact that levels of sodium in the original interstitial water are extremely high; consequently, a small sodium level flux in the leaching fluids will not significantly affect the overall migration.

362. As the experiment progressed, the migration trends of potassium in the interstitial water of dredged material seemed to decrease (Table 74 and Figure 41).

However, the overall decrease was very small, as shown in the following tabulation:

| Column | Pore Volume of Dredged Material (ml) | Overall Applied Solution (ml) | % Decrease of K in Interstitial Water | Overall Dilution % |
|--------|---|--|--|--------------------------|
| 11 | 32,600 | 2,050 | 17.2 | 5.9 |
| 12 | 32,600 | 1,597 | — | 4.7 |
| 13 | 32,600 | 1,940 | 17.3 | 5.6 |
| 14 | 32,600 | 1,890 | 7.4 | 5.5 |
| 15 | 32,600 | 1,792 | — | 5.2 |
| 16 | 32,600 | 1,945 | 11.7 | 4.4 |

Columns 12 and 15 showed no decrease, and the other columns showed only small decreases in potassium concentrations (7 to 17 percent). As previously suggested, dilution could be the major cause of this. The difference between the percentages of decrease in potassium and the calculated percent decrease resulting from overall dilution (as listed above) may be due to short-circuit flow. Thus, it could be concluded that the different kinds of leaching fluids used in Phase II did not have significant effects on the migration trends of potassium in the dredged material interstitial waters.

363. The migration trends of potassium in the leachates from the various columns were identical to Phase I findings, possibly due to the increase in potassium. It can be concluded that the various leaching fluids had no significant effects on the migration trend of potassium in the interfacing soils.

364. The levels of potassium in the interstitial waters or leachates from the Phase II columns were found to be in a very narrow range. This finding, in addition to the migration trend of potassium, further substantiates the

fact that the transport of potassium is independent of the type of leaching fluid used in the dredged material/leaching fluid system.

365. Phase II results (Table 75 and Figure 42) show that calcium decreased in the interstitial water at a slower rate than in Phase I. However, the migration trend for calcium was very similar in both phases of the experiment, indicating that the same kinds of mechanisms may be involved in the interstitial waters of Phases I and II.

366. The migration trends for calcium in the leachates of Phase II were different from Phase I. Throughout Phase II, decreasing amounts of calcium were found in the soil solution. (Columns 11 and 16 were the exceptions). This was probably due to the strong scavenging effect of the bicarbonate ion, exhibited as follows:

| Column Number | $[Ca^{2+}]$ (M) | $[CO_3^{2-}]$ (M) | $[Ca^{2+}][CO_3^{2-}]$ |
|---------------|-----------------------|-----------------------|------------------------|
| 12 | 7.5×10^{-4} | 8.0×10^{-6} | $10^{-8.22}$ |
| 13 | 2.48×10^{-3} | 3.05×10^{-5} | $10^{-7.12}$ |
| 14 | 1.25×10^{-3} | 1.13×10^{-5} | $10^{-7.85}$ |
| 15 | 1.3×10^{-3} | 1.47×10^{-5} | $10^{-7.72}$ |
| 16 | 6.05×10^{-3} | 1.01×10^{-5} | $10^{-7.21}$ |

If these data are compared to the solubility of calcite,

$$[Ca^{2+}][CO_3^{2-}] = \begin{matrix} 10^{-8.35} & (I = 0) \\ 10^{-6.2} & (\text{seawater condition}) \end{matrix} \quad (63)$$

it can be seen that the results of the products of $[Ca^{2+}][CO_3^{2-}]$, as listed in the tabulation are in the range of $10^{-8.35}$ to $10^{-6.2}$, indicating that calcite plays an important role in regulating calcium levels. The high values of soluble calcium in Columns 11 and 16 (both acid rainfall simulations) were probably caused by the dissolution of

calcite by the hydrogen ion. The other column leachates had higher pH values, which would promote calcite precipitation. Thus, calcium levels would be gradually reduced.

367. The migration trends and levels of magnesium, in both the interstitial water and leachates of the Houston dredged material/Perkins loam, are similar (Table 76 and Figure 43). The magnesium in the interstitial water from the rainfall simulation columns is the exception. In general, the migration trends are similar to Phase I, which indicates that the magnesium in dredged material/interfacing soil systems is usually controlled by the interfacing media; the various leaching fluids do not greatly affect the migration of magnesium.

368. In Phase II, chloride displayed many unusual migration trends and levels (Table 77 and Figure 44). For example, data from Column 11 show that chloride, like sodium, increased in the interstitial water during the leaching experiment. However, there were no data on chloride levels in the interstitial water samples from the other Phase II columns. Furthermore, there are not enough data on chloride levels to support any meaningful speculations. Another phenomenon concerns Columns 12 and 13 (rainfall and municipal leachate) which showed relatively high levels of total chloride in the leachates, while total chloride in Columns 14 to 16 decreased to much lower levels than in the other Phase II columns.

369. Since there are no data on soluble chloride, and insufficient data on total chloride, the effects of various leaching fluids on chloride levels cannot be accurately evaluated.

Trace metals

370. The migration of iron in the Phase II study was similar to that in Phase I. Strong release of particulates

of iron from the leaching media was observed. These same migration trends were also observed for total and soluble iron in the leachates from the interfacing material. Therefore, the same mechanisms that were discussed for the Phase I results are applicable to this part of the experiment.

371. In comparing the different leachates in the Houston dredged material/Perkins loam columns, the migration trends and levels of iron in these columns were similar (Table 78 and Figure 45). Leaching fluids with high initial TOC values (e.g., the municipal leachate with a TOC of 280 ppm or the fulvic acid leaching fluid with a TOC of 36 ppm) or low initial pH values caused little increase in the iron concentrations. Therefore, it seems that the leaching media were a good buffer material and could regulate iron levels regardless of changes in the leaching fluid characteristics.

372. Manganese also had similar migration patterns in Phase I and Phase II (Table 79 and Figure 46). However, the levels of manganese were lower during Phase II, with the final soluble concentrations (both in interstitial water and leachates) as low as 0.02 ppm at the time of the final sampling. All of the Phase II columns showed similar concentration and migration trends, both for the dredged material interstitial waters and final leachates. This indicates that there was no major effect on the migration of manganese in dredged material/interfacing soil systems caused by various leaching fluids. The particulate form of manganese in Column 12 (rainfall leaching fluid) was about two to three times higher than that in the other leaching columns with the same leaching media; this was probably because the leaching media were not evenly distributed and was not an effect of the leaching fluids.

373. Levels of cadmium in the interstitial water of Columns 14 through 16 were found to be higher than those of

Columns 12 and 13, during the second sampling (Table 80 and Figure 47). The increase of cadmium in the interstitial water may be caused primarily by solubilization and complexation; therefore, higher cadmium levels in interstitial water indicated that either the pH levels were lower or the chelating agents were higher. From the experimental results, it is difficult to ascertain which of these conditions existed, since the cadmium levels were usually quite low (0.003 ppm), and the concentration differences between the columns were usually quite small. Therefore, it is suggested that the various leaching fluids could not greatly affect the migration of cadmium. This can be further substantiated by the levels of soluble cadmium in the leachates as well as in the final sampling of the interstitial water. In all these instances, cadmium levels were similar. As regards total cadmium contents in the leachates, it is believed that physical scouring is the main cause of the release of cadmium-particulates; the effect caused by the different types of leaching fluids is relatively unimportant.

374. The behavior of copper in the leachate samples from the Phase II columns was also similar to those of Phase I, a decrease in copper levels as time increased (Table 81 and Figure 48). The concentrations of copper in the final interstitial water samples were all less than 10 ppb. This same behavior also occurred during the migration of copper in the soils, where different types of leaching fluids did not exert a significant influence on the trends and levels of copper transport. There was a slight difference in total copper levels in the leachates from the different columns. However, as previously discussed, this difference probably resulted from the nonhomogeneous distribution of particles in the lysimeter columns

and not from the chemical characteristics of the leaching fluids.

375. All the soluble forms of mercury in the Houston dredged material/Perkins loam were below detectable analytical levels (Table 82 and Figure 49). This was probably due to the extremely low solubility of mercuric sulfide solids. The addition of organic matter by the leaching solutions (such as Column 13 with 280 ppm TOC and Column 14 with 75 ppm fulvic acid) did not seem to significantly affect mercury migration. The acid rainfall (with a pH of 4.5) was also unable to elute the mercury from either the dredged material or soils.

376. Lead levels in Phase II were much lower than in Phase I. As discussed in the "Migration of Constituents in Dredged Material/Leaching Fluids Systems" section, lead-carbonate complexes can raise lead concentration as high as 200 to 250 ppb under the experimental conditions discussed. The results of this experiment showed very low soluble lead concentrations, to 20 ppb. As previously discussed, adsorption might be the most important factor in regulating lead levels. Due to predominant forces such as adsorption reactions, other factors, such as adding organic matter (Columns 13 and 14) or reducing pH, would not have significant effects on the lead attenuation or elution in this experimental situation (Table 83 and Figure 50).

377. The experimental results for zinc show that concentrations of both total and soluble forms of zinc in interstitial waters and leachates decreased as the time increased (Table 84 and Figure 51). The initial soluble zinc levels in the interstitial water of Houston dredged material/Perkins loam leaching tests were in the range of 0.03 to 0.08 ppm. However, at the second set of data points of the migration curves, all the zinc levels in the interstitial water were close to 0.003 ppm and remained the

same in subsequent samplings. Therefore, soluble zinc levels in the dredged material probably will not be affected significantly by different leaching fluids. In general, the migration trend of zinc in the interfacing soil (Perkins loam) was the same as in the dredged material, with a minimal variation in the initial samples. It seems that the dredged material/interfacing soil system will act as a buffer system to regulate the amended zinc level. This can be substantiated by the results of leaching conditions utilizing municipal leachate with an original zinc level as high as 15 ppm or the acid rainfall sample with a pH as low as 4.5.

Summary of the Migration of Constituents in
Laboratory Simulations of Upland
Disposal of Dredged Material

378. The preceding discussions of individual constituents will be summarized in this section of the report which is divided into three subsections that coincide with the report sections. The experimental phenomena and controlling mechanism for each parameter are listed; for definitions of terms, refer to the "Glossary."

Migration of constituents in
dredged material/leaching
fluid systems

379. The summary of the experimental results and controlling mechanisms of the migration of constituents in dredged material is presented in the following tabulation:

| <u>Parameter</u> | <u>Experimental Phenomena</u> | <u>Controlling Mechanisms</u> |
|------------------|---|--|
| pH | Values of pH in the interstitial water approached 8, from original values of about 6.7. | Hydrogen ion concentration of the interstitial water was decreased by less bioactivity, dilution, and dissolution of calcite; the final levels could be regulated by calcite through the following reaction: $\text{CaCO}_3(\text{S}) + \text{H}^+ = \text{HCO}_3^- + \text{Ca}^{2+}$ |

| <u>Parameter</u> | <u>Experimental Phenomena</u> | <u>Controlling Mechanisms</u> |
|--------------------|---|--|
| Eh | <p>Dredged material with larger particle sizes showed higher Eh values throughout experiment.</p> <p>After leaching, the Eh values were slightly increased.</p> | <p>Diffusion of oxygen from the atmosphere, which is affected by the porosity of the dredged material.</p> <p>Leaching fluid flow rate (TOC content in dredged material was somewhat important though less than the flow rate).</p> |
| TOC | TOC levels increased from about 100 ppm to 300 to 600 ppm in six months of experimentation. | <p>Solubilization of organic matter from dredged material;</p> <p>Biodegradation.</p> |
| Alkalinity | Alkalinity levels were gradually increased in the interstitial water throughout the experimentation. | <p>Dissolution of carbonate solids due to acid production (from oxidation of organic matter);</p> <p>Dissolution of carbonate solids due to the metal transformation (calcite was the main solid for the release of alkalinity).</p> |
| NH ₃ -N | The concentrations of ammonia-nitrogen in interstitial waters were found to decrease throughout the leaching test. | <p>Redox state (higher redox potentials were less favorable to the accumulation of ammonia in interstitial water);</p> <p>Dilution (flow rate);</p> <p>Reaction flux (total nitrogen in dredged material).</p> |
| TKN | The concentration of total Kjeldahl nitrogen was found to decrease throughout the experiment. | <p>Redox state (affects solubilization);</p> <p>Bioconversion;</p> <p>Dilution.</p> |

| <u>Parameter</u> | <u>Experimental Phenomena</u> | <u>Controlling Mechanisms</u> |
|--------------------|--|--|
| Ortho- and total P | Both orthophosphate and total phosphorus were quite low in the interstitial waters. At the conclusion of the experiment the levels of phosphorus approached 0.01 ppm. | Mainly controlled by the solubility of calcium phosphate solids. |
| Na ⁺ | Sodium in the interstitial water was found to decrease gradually throughout the experiment. | Dilution effect. |
| K ⁺ | Potassium in the interstitial water decreased gradually throughout the experiment. | Dilution effect. |
| Ca ²⁺ | The calcium levels in interstitial water changed slowly, increasing slightly during the initial experiment, decreasing throughout the remainder of the experiment. | Solubility effect (controlled by calcite); pH and carbonate levels. |
| Mg ²⁺ | Saline or brackish dredged material, the magnesium levels exhibited either no significant changes or increased only slightly then decreased again after 1 to 2 months of leaching. | Solubility effect or solid-solution effect (controlled by nesquehonite and/or dolomite). |
| | In freshwater dredged material the levels of magnesium continually decreased throughout the experiment. | Dilution effect. |

| <u>Parameter</u> | <u>Experimental Phenomena</u> | <u>Controlling Mechanisms</u> |
|------------------|---|---|
| Cl^- | <p>In saline dredged material, the soluble chloride values changed only slightly (either increased or decreased) after the leaching test.</p> <p>At the end of the experiment in freshwater dredged material, the soluble chloride values decreased about 50 to 65 percent over the initial values.</p> | <p>Ion exchange effect.</p> <p>Dilution effect.</p> |
| Fe | <p>The soluble iron in interstitial water exhibited a decrease-increase-decrease-increase cycle. The final levels of iron (after six months) were about 0.5 to 0.8 ppm for the salt-water dredged material and decreased to nil for the freshwater dredged material.</p> | <p><u>Trend</u>: Controlled by solid transformation (formation of $\text{Fe}(\text{OH})_3$ and FeOOH solids), complexation effects, and redox potential.</p> <p><u>Level</u>: Controlled by the formation of iron-organic complexes.</p> |
| Mn | <p>In general, soluble manganese levels increased in the initial period of leaching (within two months) and decreased throughout the remainder of the experiment.</p> | <p><u>Trend</u>: Controlled by solid transformation (conversion from MnS to MnCO_3 and then to MnOOH or Mn_xO_y solids) and redox potential.</p> <p><u>Level</u>: Complexation effect (formation of Cl^- and HCO_3^- complexes).</p> |
| Cd | <p>In general, cadmium in the interstitial water was found to increase in the initial experimental period (2 to 3 months) then decrease.</p> | <p><u>Trend</u>: Changes in solubility of controlling solids (probably from sulfide solids to carbonate solids);</p> |

| <u>Parameter</u> | <u>Experimental Phenomena</u> | <u>Controlling Mechanisms</u> |
|------------------|---|--|
| | | <p>Adsorption by hydrated oxides of iron and manganese with Eh increase.</p> <p><u>Level</u>: Formation of cadmium-organic and cadmium-chloride complexes and Cd^{2+} free ion.</p> |
| Cu | <p>Soluble copper levels were significantly decreased after about 3 months of the experiment. The final concentration (after 6 months) of copper in the interstitial water was less than 3 ppb (originally 10 to 70 ppb).</p> | <p><u>Trend</u>: Solid transformation (from CuS to $\text{Cu}_2\text{CO}_3(\text{OH})_2$);</p> <p>Adsorption by hydrated oxides of iron and manganese;</p> <p>Dilution effect.</p> <p><u>Level</u>: Complex formation (Cu-CO_3, $\text{Cu-B}(\text{OH})_4$ and/or copper-organic complexes).</p> |
| Hg | <p>Soluble mercury levels in interstitial waters were maintained at a constant level after 1 month of experimentation (concentration usually less than 1 ppb).</p> | <p><u>Trend</u>: Initially by the low solubility of $\text{HgS}(\text{s})$;</p> <p>Throughout experiment, adsorption by hydrated oxides of iron and manganese.</p> <p><u>Level</u>: Mercury-organic complexes.</p> |
| Pb | <p>The soluble lead levels in interstitial waters of saline dredged material were generally increased to the levels of 250 to 300 ppb.</p> <p>In freshwater dredged material the soluble lead generally decreased from about 30 ppb to below 1 ppb.</p> | <p><u>Trend</u>: Transformation from $\text{PbS}(\text{s})$ to $\text{PbCO}_3(\text{s})$;</p> <p>For saline dredged material, lead-carbonate or lead-organic complexes can account for the levels analyzed.</p> <p>Adsorption effect (hydrated iron oxide);</p> <p><u>Level</u>: For freshwater dredged material, adsorption effect kept the levels low.</p> |

| <u>Parameter</u> | <u>Experimental Phenomena</u> | <u>Controlling Mechanisms</u> |
|--------------------------|---|---|
| Zn | There were two transport trends: (1) Zinc was decreased as the experiment progressed, and (2) in the interstitial water, zinc suddenly increased and then decreased again. The final level of zinc was in the range of 1 to 20 ppb (six months of experimentation). | <u>Trend:</u> Controlled by zinc-silicate or zinc-clay minerals through solubility or adsorption effects; <u>Level:</u> Zinc-OH ⁻ complexes and zinc-organic complexes. |
| Chlorinated Hydrocarbons | The levels of chlorinated hydrocarbons were extremely low (below detection limits). | Adsorbed by dredged material particles, such as clay minerals, iron and manganese-hydrated oxides and organic matter. |

380. From these summaries, it can be seen that the migration of constituents in dredged material/leaching fluid systems is very complicated. No single mechanism can account for the trends and levels of migration of various constituents. Among the controlling factors, the following are of major concern:

- a. Physical effect. The physical effect can produce changes in Eh, sodium, potassium, magnesium, and chloride. Except for Eh, the principal physical effect is dilution, which is related to the flow rate of the leaching solution and the pore volume of the dredged material and can usually decrease the concentration of constituents in the interstitial water. Eh is mainly affected by the diffusion of oxygen, which can increase the Eh levels in interstitial water.
- b. Solubility effect. The solubility effect can change the levels of calcium, magnesium, pH, alkalinity, phosphorus, as well as all the trace metals in the interstitial waters. This effect is controlled principally by the by-products of bacterial activity and the input of oxygen to the system. Two major by-products are carbon dioxide

and hydrogen sulfide. The former can influence levels of alkalinity, pH and calcium through dissolution and/or precipitation of calcite. The combination of carbon dioxide and hydrogen sulfide was the major factor for regulating the redox condition. After the redox conditions were developed, redox potential could change the solid species of metals and regulate the trend of metal migration. The solubility effect is also influenced by the types and levels of anions in the interstitial waters.

- c. Complexation effect. The complexation effect usually accounts for the high level of trace metals in the interstitial water. From the literature survey, as well as the results of this research, the following complexes were found to account for the trace metal results:
- Cd - organic and chloride complexes
 - Cu - organic, carbonate, and borate complexes
 - Fe - organic complexes
 - Hg - organic and chloride complexes
 - Mn - chloride and bicarbonate complexes
 - Pb - carbonate and organic complexes
 - Zn - hydroxide and organic complexes.
- d. Adsorption effect. The adsorption effect explains the low levels (lower than those controlled by the solubility effect) of trace metals and chlorinated hydrocarbons in the interstitial waters. It could also modify the trends of trace metal migration. In this experimental system, it is suggested that the most important adsorbents were hydrated oxides of iron and manganese as well as various clay minerals.
- e. Hydrolytic effect. The hydrolytic action on complex organic matter was one of the most important factors for the release of soluble organic carbon and nitrogen compounds.
- f. Redox reaction. Redox reactions in this experiment were especially important for the transformation of nitrogen compounds in the interstitial waters. It also affected the transformation of metal solids.
- g. Ion exchange effect. Ion exchange effect controlled the changes of chloride levels in the interstitial water.

Migration of constituents in
interfacing soil/leaching
fluid systems

381. The experimental phenomena and controlling mechanisms of constituents in soils observed in this study are summarized in the following tabulation:

| <u>Parameter</u> | <u>Experimental Phenomena</u> | <u>Controlling Mechanisms</u> |
|------------------------|---|---|
| pH | Lake Arrowhead: decreased from about 8 to about 6.9; Perkins: decreased from about 8 to about 7.7. | Due to the strong release of Ca^{2+} from soil: $\text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{H}^+ + \text{CaCO}_3(\text{s})$; pH values were regulated by $\text{CaCO}_3(\text{s})$; Depression of pH by weak acids present in soil; Oxidation reaction. |
| TOC | Lake Arrowhead: TOC levels were either released from soils or kept unchanged by dredged material leachates. Perkins: TOC levels were usually released from soils by dredged material leachates. | The release of TOC was due to dissolution, complexation, bioreaction, and sorption. |
| Alkalinity | Alkalinity levels in dredged material/interfacing soil leachates gradually decreased to levels in the soil control columns. (Lake Arrowhead sandy loam ranged from 350 to 500 ppm and Perkins loam from 1200 to 1500 ppm as calcium carbonate.) | Regulated by the precipitation reaction of calcium carbonate. |
| $\text{NH}_3\text{-N}$ | Initially: Ammonia was decreased by soil. Remainder of experiment: Ammonia either decreased | Adsorption; Bioconversion (ammonification or nitrification). |

| <u>Parameter</u> | <u>Experimental Phenomena</u> | <u>Controlling Mechanisms</u> |
|----------------------------|---|---|
| NH ₃ -N (cont.) | or was released at low levels by soils. | |
| TKN | The total Kjeldahl nitrogen was increased in soil leachates by the disposal of dredged material on the soil. | Bioconversion; Solubilization (hydrolytic actions). |
| Ortho- and Total P | Phosphate showed an initial release from the soil into the solution in the control sets. After six months of experimentation, the phosphate levels were decreased to trace levels in most columns. Soluble phosphate levels in other columns showed extremely low levels throughout the experiment. | Phosphate might be released due to the reduction of FePO ₄ (s) or the reduction of hydrated oxides of iron and manganese adsorbents. However, released phosphate could be scavenged by the highly soluble calcium ion. |
| Na ⁺ | Sodium could be eluted from Perkins soil. After percolating through the soils by dredged material leachates, the attenuation of sodium was observed. For high sodium leaching fluids, the attenuation capacity of soils gradually decreased as leaching time increased. | <u>Attenuation:</u> Ion exchange mechanism (exchange for Ca ²⁺); <u>Elution:</u> Dissolution of simple sodium-solids from Perkins soil; Ion exchange. |
| K ⁺ | Potassium could be eluted out from the soils. There was no overall mass removal of potassium by soils. | Dissolution of simple potassium solids from dry soils; Ion exchange reactions. |
| Ca ²⁺ | Calcium was strongly released from soils by the leaching solutions. The releasing rate was higher in saline dredged material/soil tests than that in freshwater dredged material/soil tests. | <u>Source:</u> Ion exchange by sodium and magnesium ions. <u>Level:</u> Regulated gradually by calcite (CaCO ₃). |
| Mg ²⁺ | Magnesium was strongly attenuated by soil. The attenuation capacity was | <u>Source:</u> Ion exchange (replaces the Ca ²⁺ ions on the clay minerals). |

| <u>Parameter</u> | <u>Experimental Phenomena</u> | <u>Controlling Mechanisms</u> |
|------------------|---|--|
| | decreased as the experiment increased. | <u>Level:</u> Regulated by available exchange sites. |
| Cl ⁻ | Either attenuation or elution could occur depending on the relative levels of chloride in the leaching solution from the dredged material and soils. | <u>Attenuation:</u> Ion exchange. <u>Elution:</u> Ion exchange; Dissolution (from Perkins soils only); Dilution. |
| Fe | Soluble iron was released from soils. The amount released was related to the soluble TOC levels in the leachates, the CEC of soils and the organic content of soils; A large amount of iron colloids were released from soils. | Mainly complexation (iron-organic complexes); pH, Eh, and ion exchange also could affect the release; Colloidal iron elution: physical scouring effect. |
| Mn | The amount of soluble manganese released from Lake Arrowhead soil was significant. The migration of manganese in Perkins soil was relatively low. | Solubilization (solubility controlling solid(s) were transformed gradually from oxides or hydrous oxides to carbonate and sulfide); Complexation (formation of chloride and organic complexes). |
| Cd | Cadmium was eluted from soils by distilled water; In general, soluble cadmium in the leaching solution was removed by soil. | <u>Trend:</u> Dissolution of CdCO ₃ (s) and cadmium-inorganic complexes formation, <u>Level:</u> Levels in the control set are mainly from cadmium-chloride complexes, <u>Trend:</u> Precipitation (solid transformation gradually from CdCO ₃ to CdS), adsorption and decomplexation effects, |

| <u>Parameter</u> | <u>Experimental Phenomena</u> | <u>Controlling Mechanisms</u> |
|--------------------------|---|--|
| | | <u>Level:</u> Cadmium levels are due to cadmium-chloride and cadmium-organic complexes. |
| Cu | <p>Soluble copper could be released in the range of 1 to 5 ppb from soils by distilled water.</p> <p>Soluble copper could be attenuated by soil, if the influent levels were greater than 5 ppb, which usually occurred in the beginning experimentation.</p> <p>A large quantity of particulate bound copper were leached out in the initial period of the experiment.</p> | <p>pH and complexation effects.</p> <p>pH, Eh, complexation (by insoluble organic matter);</p> <p>Precipitation (sulfide solids);</p> <p>Adsorption (clay minerals, iron, and manganese colloids);</p> <p>Physical scouring.</p> |
| Hg | <p>There was little difference in the soluble mercury in the influent solutions to soils and resulting leachates.</p> <p>Particulate mercury was found to be released into the leachates.</p> | <p>The equilibrium state of solubility adsorption and complexation was reached.</p> <p>Physical scouring.</p> |
| Pb | <p>Lead was removed by soils. The attenuation capacity of soils on lead was gradually decreased as leaching time increased.</p> | <p>Adsorption (clay minerals, iron and manganese colloids);</p> <p>Solubilization (due to sulfide solid formation).</p> |
| Zn | <p>Zinc was usually eluted in the experiment.</p> | <p>High zinc-organic complexation capacity and relatively low adsorption and sulfide formation capacities.</p> |
| Chlorinated Hydrocarbons | <p>Chlorinated hydrocarbons were found either associated strongly with soil</p> | <p>Strong adsorption capacity between chlorinated hydrocarbons</p> |

| <u>Parameter</u> | <u>Experimental Phenomena</u> | <u>Controlling Mechanisms</u> |
|------------------|--|-------------------------------|
| | particles or they would not leach into the soil-solution at all. | and solid particles. |

382. From the preceding summaries, it can be seen that the attenuation of soluble constituents by soils was usually governed by adsorption, deposition, or ion exchange. However, the elution of soluble constituents was usually regulated by dissolution, desorption, ion exchange, complexation, bioconversion, and hydrolytic actions. Physical scouring was the principal mechanism for the initially large release of many total leachate constituents from the soils.

383. Adsorption was very important for the removal of ammonia-nitrogen, cadmium, copper, mercury, and lead from the soil solution. As suggested for the dredged material/water system, the main adsorbents for the soil/water system were also probably hydrated oxides of iron and manganese, clay minerals, and insoluble organic matter. Deposition was important for the control of pH, alkalinity, phosphorus, and some of the trace metals. Ion exchange was related to the migration of major ions such as sodium, potassium, calcium, and magnesium. In this experiment, calcium and potassium were usually replaced by high levels of sodium and magnesium.

384. Dissolution of metallic solids became significant when solid transformation occurred; iron and manganese were prime examples of this effect. Throughout the experiment, these two metals were most probably transformed from low-solubility, high oxidation state solids in the aerated soil to high-solubility, low oxidation state solids when the soils were buried and flooded. The latter promoted a greater release of soluble forms.

385. Complexation was important for the release of trace metals into the soil solution. The organometallic

complexes are believed to be the most significant species in accounting for the levels of metals analyzed. Therefore, the bioconversion and hydrolytic reactions of organic matter were often the most plausible causes for the strong release of metals. In general, in this experiment the desorption mechanism was relatively unimportant for the release of soluble constituents.

Effects of various leaching fluids
on the migration of constituents
in dredged material/interfaces
soil systems

386. The experimental results of the effects of various leaching fluids on the migration of constituents in dredged material/interfaces soil systems show that:

- Dredged material and soil are important reservoirs and/or sinks for various constituents, i.e., the effects by various leaching fluids were usually negligible.
- The controlling mechanisms for the migration of constituents which were affected by environmental conditions were mainly regulated by dredged material or soil, and not by the various leaching fluids.

As a result, the effects of various leaching fluids on the migration of constituents were limited. Only the migration trends or levels of a few parameters, TOC, alkalinity, and soluble calcium, were altered by the unusual characteristics of the leaching fluids.

387. TOC in the leachate from the municipal leaching fluid lysimeter column (Column 13) was found to be significantly higher than in the other columns. This might be due to the fact that TOC was usually eluted from dredged material and interfacing soils (as discussed in the preceding sections). No significant mechanism could remove the high input of TOC (280 ppm) from the municipal leachates. Therefore, in comparing low TOC leaching fluids to leaching fluids with significantly higher TOC levels, a higher release of TOC could result.

388. As was discussed, alkalinity levels could be decreased by interaction with an interfacing soil. However, it was found that if the pH of the leaching fluid was low (e.g., acid rainfall simulation), the alkalinity removing capacity of the soil was significantly decreased because the alkalinity removal was usually from the precipitation of calcite:



Therefore, if the leaching fluids had a low pH value, the above reaction could be inhibited.

389. In this test, calcium concentrations in leachates usually decreased. However, after a long period of leaching (three months), calcium was eluted from the columns being fed with an acid rainfall leaching fluid. Just as for the alkalinity increase, the increase of calcium was primarily from the dissolution of calcite in the leaching media.

Potential Impact on Water Quality of Leachates from Upland Dredged Material Disposal Sites

390. A potential environmental impact associated with the upland disposal of dredged material is degradation of groundwater by leachate. If the hydrogeological regime of the disposal area is such that groundwater impacts surface water, then leachates may cause degradation of both saline and fresh surface waters.

391. The purpose of this section of the report is to compare the experimental results from the lysimeter columns with existing and/or proposed water-quality standards/regulations to evaluate the potential for water contamination. It has been divided into three subsections as follows:

- Water-quality criteria
- Comparison between experimental results and existing water-quality criteria; and

● Potential impact of dredged material leachates. The first subsection will present potentially applicable water-quality criteria; the second will compare the levels of constituents in the experimental leachates to these criteria; and the final subsection will evaluate the potential impact of constituents in dredged material leachates. Water-quality criteria

392. Thus far there are no regulations specific to the control of leachates from dredged material disposal sites. With this in mind, the experimental leachate results from Phase I of the subject study are compared to five criteria (presented in Table 91), as follows:

- Public water supply
- Fresh water (aquatic life)
- Agriculture water (irrigation)
- Marine water (aquatic life); and
- Groundwater.

393. Within each criterion are water-quality limits from several entities: the Environmental Protection Agency (EPA), National Academy of Science (NAS), National Technical Advisory Committee (NTAC), and various state agencies (129, 130, 131, 132).

394. Public water supply criteria have been included in this discussion because groundwater aquifers are a source of drinking water for many municipalities. Criteria for fresh water and saline water as receiving water bodies have been included since, theoretically, groundwater that has been contaminated by dredged material leachates can be discharged into surface waters. It should be noted that the various criteria are compared to values of contaminants in the leachates without any dilution by receiving groundwater. Agricultural water criteria have been included for comparison since, at times, major groundwater aquifers may be used to supply water for irrigation purposes.

395. The Federal Water Pollution Control Act of 1972 (Public Law 92-500) established the framework for

water-quality control laws and regulations in the states. Under this law, the states retain the primary responsibility for water-quality protection. However, the Federal EPA is authorized to intervene if the states do not enforce the law.

396. All states administer a water-quality standards program wherein the surface waters of the state are categorized by beneficial uses, e.g., drinking water supply, recreation, fish and wildlife, agricultural, and industrial. For each class of water use, narrative and/or numerical limits are established for various parameters. To protect its beneficial uses, the parameter limits are to be maintained in the receiving water.

397. Public water supply criteria. EPA is authorized by the Safe Drinking Water Act of 1974 to establish drinking water standards. The important parameters developed under this law are listed in Table 92. The numerical values are compiled from the EPA National Interim Primary Drinking Water Regulations (40 CFR 141; 40 FR 59565, December 24, 1975; Amended by 41 FR 28402, July 9, 1976) and EPA National Secondary Drinking Water Regulations (40 CFR 143, March 31, 1977). The NAS and NTAC public water supply criteria levels are also listed in the same table for purposes of comparison (130, 131, 132).

398. Freshwater (aquatic life) criteria. The water-quality criteria for freshwater aquatic life is delineated in Table 92. Since upland dredged material disposal sites are usually close to natural waters (including inland rivers or lakes), there is a possibility for dredged material leachates to contaminate fresh water bodies. There are several freshwater criteria in existence for aquatic life, wildlife, or recreational waters. Only the water-quality criteria for aquatic life are listed in Table 92 since among the above-mentioned uses, the criteria for aquatic life are the most strict.

399. Irrigation water criteria. Since dredged material leachates may also contaminate surface or groundwater to be used for irrigational purposes, the irrigation water criteria are also listed in Table 92 for comparison (129). The regulation of irrigation water quality must take into consideration the short-term effects on crop quality, long-term effects on soil characteristics and surrounding groundwaters, and the intended use of the crop. Water classified as irrigation water is generally applied to (1) agricultural crops, (2) pasture land, (3) turf and landscape, and (4) stock watering. Absolute limits on irrigation water are difficult to establish due to a number of site-specific factors, e.g., soil type, climate, irrigation practices, etc.

400. Table 92 presents general limits for irrigation water constituents, as suggested by EPA, NAS, and NTAC for both short-term and extended (over 20 years) use.

401. Marine water-quality criteria (aquatic life). Four kinds of marine water-quality criteria for aquatic life are included in Table 92, i.e., criteria from EPA, NAS, NTAC, and the state of California (129, 133). Since the dredged material leachates may enter marine water, the marine water-quality criteria must also be examined in evaluating the potential impact of the leachates.

402. Groundwater protection criteria. In nearly all cases, state regulatory agencies are authorized to protect both surface and subsurface waters, e.g., to prevent degradation of groundwater. However, only a few states currently have specific criteria for groundwater protection.

403. The Maryland Groundwater Quality Standards (Reg. 08.05.04.04), for example, identify three types of underground aquifers -- Types I, II, and III -- based on transmissivity, permeability, and total dissolved solids concentration of the natural water. The following limitations have been established for each type:

a. Type I Aquifers

The characteristics of constituents of waters or wastewaters discharged into Type I Aquifers may not exceed, or cause the natural groundwater quality to exceed, mandatory or recommended standards for drinking water as established by the Federal Government.

b. Type II Aquifers

The characteristics or constituents of waters or wastewaters discharged into Type II Aquifers may not exceed or cause the natural groundwater quality to exceed receiving (surface) water quality standards as established for Class I Waters by the State. In addition, the person responsible for the discharge shall provide the Water Resources Administration with evidence that the discharge will not result in pollution of Type I Aquifers.

c. Type III Aquifers

The characteristics or constituents of waters or wastewaters discharged into Type III Aquifers shall be identified to the Water Resources Administration, and evidence shall be provided to assure the Water Resources Administration that there will not be pollution of either Type I or Type II Aquifers or surface waters, and that the public health and welfare will not be endangered as a consequence of such disposal.

404. According to the New York Groundwater Classification and Standards (Part 703):

The ground waters of the State are classified according to best use, and all fresh ground waters are best used as sources of potable water supply. Such fresh waters, when subjected to approved disinfection treatment and/or additional treatment to reduce naturally present impurities to meet New York State Health Department drinking water standards, are deemed satisfactory for potable purposes.

Contaminant limits established in New York for groundwaters to be used as a potable water supply are shown in Table 92.

405. The state of Missouri has Regulations for Groundwater Recharge and Irrigation Return Water, as follows:

This section shall apply to percolating water from all areas of land on which wastes or wastewater is applied or allowed to accumulate whether or not

additional treatment is to be obtained by application to the land. Such percolating water shall be considered an effluent to the subsurface "Waters of the State" when it reaches a depth of more than 4 feet or is within 12 inches of bedrock if such bedrock occurs at depths of less than 5 feet, and shall be subject to the following requirements. Percolating water which is intercepted by either natural or artificial means and reappears on the surface shall be considered indirect release to surface "Waters of the States..."

The specific requirements for Missouri state groundwater contaminant limits are delineated in Table 92.

406. Kansas has Underground Storage Regulations that require a permit for all surface ponds. The regulations apply as follows:

This article regulates the construction and use of underground storage reservoirs and the construction and use of disposal wells and surface ponds for the confinement, storage and disposal of industrial fluids including but not limited to brines, but does not include regulations pertaining to oil field activities described in L 1965, Ch. 506, Sec 1(4)p.

407. The Kansas Regulations also state the following regarding operation and maintenance:

Operators of underground reservoirs shall maintain a permanent record of the type and quantity of all products stored therein, and a continuous record of the injection pressures, and shall report immediately to the chief engineer for the State Board of Health any failures or defects in the underground reservoir.

408. The Idaho regulations have a section on Land Treatment and/or Disposal of Wastewater(s), shown below:

Land treatment and/or disposal liquid material requires that...Provision shall be made for monitoring the quality of the ground water in proximity of the disposal area. All data and reports resulting from the ground water monitoring program will be submitted to the Department upon request. The minimum frequency of monitoring and data submittal will be determined by the Department and in general will be dependent upon the nature and volume of wastewater material, the frequency and duration of disposal, and the characteristics of the soil mantle on the disposal site. Land treatment and/or

disposal shall not create a ground water mound or result in a salt build-up on another person's property. Land treatment and/or disposal shall not create a public health hazard, a nuisance condition, or an air pollution problem.

409. The Michigan Liquid Industrial Waste Disposal Act governs the methods of disposal of liquid industrial wastes and includes licensing of persons and vehicles. It states the following regarding disposal:

...The licensee shall not dispose of wastes onto or into the ground except at locations specifically approved by the commission ... No waste shall be placed in a location where it could enter any public or private drain, pond, stream or other body of surface or ground water.

Comparison between experimental results and existing water quality criteria

410. The experimental results of the constituents in dredged material leachates are listed numerically with the previously discussed criteria (Table 97). These criteria would only be applicable to dredged material leachates if they were somehow discharged to different receiving waters. The average and maximum levels of the leachate constituents are discussed in relation to appropriate water-quality criteria in the following paragraphs.

411. pH. In all the water-quality criteria listed, pH has a widely acceptable range, with a majority of acceptable values falling between 6.5 and 8.5. The ocean discharge criteria of the state of California limit pH discharges to 0.2 units deviation, after dilution, from the naturally occurring pH of marine waters.

412. The average pH levels in the dredged material leachates were in a relatively narrow range, from about 6.8 to 7.9. These levels are well within those of the previously discussed criteria. Therefore, the pH of dredged material leachates should not become a potential problem if leachates reach natural water systems.

413. TOC. Traditionally, biochemical oxygen demand (BOD) has been a measure of the extent of organic contamination in water bodies. The very nature of dredged material, however, makes BOD inadequate.

414. Thus far, there are no criteria for TOC levels in receiving waters. However, due to the strong complexing capability between organic matter and trace metal contaminants, the levels of organics in leachates (TOC) may become most important in predicting potential increase of mobile inorganic material to potentially toxic levels. Therefore, the potential contamination problem to be caused by TOC cannot be overlooked.

415. The TOC levels in the dredged material/soil leachates in this test were significantly higher than most of the background TOC levels in natural waters. In freshwater bodies one typically encounters concentrations of a few parts per million, but occasionally (e.g., in bog or swamp waters) concentrations may be as high as 50 ppm (28). In the oceans the concentrations of TOC range from 0.1 to 10 ppm, with an average value of about 1 ppm in the surface water and lower values in deep water (10, 84, 86, 87, 88, 134, 135, 136). In this test, the average soluble TOC levels in the leachates were in the range of 250 to 440 ppm. The maximum soluble TOC in the leachates reached as high as 770 ppm, and these levels could cause contamination problems.

416. Alkalinity. With the exception of fresh water for aquatic life, there are no regulatory criteria for alkalinity levels; both EPA and NAS criteria indicate that the discharge of wastewaters into fresh water (for aquatic life) should not increase the alkalinity of natural water over 75 percent above the natural background levels. As discussed by Stumm and Morgan, the average alkalinity level in rivers is about 50 ppm as calcium carbonate and the range is about 20 to 400 ppm (as calcium carbonate) (28). However, in this experiment, the average alkalinity levels in different

leachates were in the range of 240 to 754 ppm (as calcium carbonate). Such high levels of alkalinity may exceed the EPA and NAS criteria if the alkalinity level in the receiving water exists in the average ranges discussed by Stumm and Morgan (28) and the levels in the leachates reach natural water bodies undiluted.

417. Ammonia-nitrogen. The average ammonia-nitrogen level in the Grand Haven and Mobile dredged material leachates was about 2 ppm. For the Seattle and Sayerville dredged material leachates, the average values were in the range of 3.5 to 5 ppm. The highest ammonia-nitrogen value found in this experiment was 13.3 ppm.

418. Comparing the experimental results to existing criteria, it can be found that the dissolved ammonia in the leachates was higher than the receiving water criteria (about 0.5 ppm; some 7 to 10 times lower than in dredged material leachates). Therefore, in order to keep the ammonia at acceptable levels, the dilution factor of the receiving water should be greater than a factor of 7 to 10.

419. The state of California has effluent quality requirements for soluble ammonia in ocean discharges: the ammonia-nitrate should be kept less than 40 ppm for 50 percent of the time and 60 ppm for 10 percent of the time. These criteria are based on a dilution factor of 200. Thus, it appears that the ammonia level will probably not become the limiting factor for potential discharge of dredged material leachates to ocean waters if a sufficient dilution factor can be obtained.

420. Nitrate-nitrogen. The average nitrate-nitrogen level in the Grand Haven and Sayerville dredged material leachates was about 12 ppm; in the Seattle dredged material leachates, it was about 1 ppm. The maximum nitrate-nitrogen levels for the former were about 30 to 34 ppm, and for the latter, about 4 ppm. From the experimental results, it can be seen that the nitrate levels in the leachates from the

Seattle dredged material/soil are acceptable. However, other leachates may violate the groundwater contaminant limits of the states of New York and Missouri. The levels of nitrate may also exceed the EPA, NAS, and NTAC public water supply criterion for nitrate. Nitrate in dredged material leachates may pose public health problems, should the leachates reach aquifers that are used for potable water supplies.

421. Phosphorus. In this experiment both total and soluble phosphorus were found in very low levels in the dredged material leachates. When compared to appropriate criteria, it appears from this study that leachates from dredged material will probably not cause problems with eutrophication in impounded water.

422. Cadmium. The cadmium limit in public water supply set by EPA, NAS, and NTAC is 100 ppb; the limit in waters for other beneficial uses is more strict, usually in the range of 5 to 50 ppb.

423. The average soluble cadmium level in the dredged material leachates was about 2 to 19 ppb; the average total cadmium level could increase from about 4 to 30 ppb. These levels are lower than the criteria for public water supplies, but may exceed other related criteria, such as for fresh water (aquatic life), irrigation water, marine water, and groundwater. However, most of these criteria are based on levels in receiving waters and the majority of the cadmium data from the experimental results were lower than 30 ppb. In a practical situation, if the dilution factor is higher than 2, the pollution problems caused by cadmium in dredged material leachates can probably be avoided.

424. Copper. In all the criteria delineated in Table 92, there are higher acceptable values for copper than cadmium, with a majority higher than 200 ppb. The copper contamination limit for groundwater in Missouri alone has very strict limitations, with a maximum value of 30 ppb.

425. Soluble copper levels in the dredged material leachates were usually less than 10 ppb; the highest was 27 ppb in the Seattle dredged material/Lake Arrowhead soil leachates, which is still lower than the Missouri groundwater criteria. The total copper concentration in leachates had an average value in the range of 8 to 68 ppb, well within the criteria, except for the Missouri limitation. During the whole experimental period, there were only a few data points of total copper concentration that exceeded 200 ppb, and as the experiment progressed, the total copper levels gradually decreased to levels similar to the soluble copper levels. Therefore, it is concluded that copper in dredged material leachates will probably not cause contamination problems.

426. Iron. The maximum contaminant level for iron in public water supplies proposed by EPA, NAS, and NTAC, was 0.3 ppm, based on the possible aesthetic effects. For marine water (aquatic life) and groundwater quality control, the tolerable level for iron is also usually 0.3 ppm. However, the limit of iron in the waters utilized for irrigation purposes can be as high as 5 ppm.

427. As previously discussed, iron levels in the dredged material leachates were extremely high; the average soluble levels, for the most part, were higher than 5 ppm and exceed all existing criteria.

428. Mercury. The criteria for mercury in public water supplies is 2 ppb. The ocean discharge standards for mercury in California are 1 ppb for less than 50 percent of the time and 2 ppb for less than 10 percent of the time. Other criteria have a higher acceptable range, either 100 or 200 ppb depending on the water use.

429. The average soluble mercury levels in the leachates were less than 1 ppb; only three data points showed higher values than 2 ppb for soluble mercury throughout the entire experiment. This means the soluble mercury in

leachates generally will not become a contamination problem. However, the average total mercury content in the dredged material leachates was 3 to 5 times higher than the public water supply criteria. It is acceptable to discharge these levels of mercury to fresh water (for aquatic life), agriculture water (for irrigation), groundwater, and other marine water under the regulations of EPA, NAS, NTAC, and the states of New York and Missouri.

430. Manganese. The contaminant limits for manganese are less than 2 ppm, with the majority falling lower than 0.2 ppm. Data of this experiment show that the minimum average manganese level in the leachates was 13.3 ppm, while the highest soluble manganese level may be as high as 125 ppm. The total manganese levels were slightly higher than the soluble levels. From the experimental results, it can be seen that manganese levels exceed all existing criteria throughout the experimental period. Hence, manganese may become one of the most important factors for the restriction of dredged material leachate discharge.

431. Lead. Recommended criteria for lead in public and groundwater are usually 50 ppb. For fresh water (for aquatic life) the lead criteria are more restrictive, with a value of 30 ppb. For marine water discharge in the state of California, the limit is 100 ppb for 50 percent of the time and 200 ppb for 10 percent of the time. Water used for irrigation can tolerate a lead level as high as 5,000 ppb.

432. With the exception of the Seattle dredged material leachates, the soluble lead concentrations in this experiment were lower than the recommended criteria. However, total lead values in leachates could violate the criteria in many cases (Table 92). From the leaching trend of lead, it was seen that lead levels in leachates continually increased due to the high level of lead in dredged

material/interstitial waters and the decreasing attenuative capacity of soils. Therefore, it is expected that more lead can be leached to a receiving water body as the retention time of dredged material on soils is increased. The potential contamination problem caused by lead may become serious in the long term.

433. Zinc. Zinc is an essential and beneficial element in human metabolism; the limitation in public water supplies is as high as 5,000 ppb. No dredged material leachate results for zinc exceeded the public water supply criteria.

434. The proposed limit for zinc in the irrigation water is also very high (2,000 to 5,000 ppb). Only one data point (2,240 ppb for the total zinc content in Mobile dredged material/Lake Arrowhead soil) was higher than the limitation. There were only a few cases in which the zinc in the dredged material leachates could be released in concentrations higher than the ocean discharge criteria of California. However, many data points of zinc show leachate levels of zinc not acceptable to the EPA marine water criteria (for aquatic life) and the state of Missouri groundwater contaminant limits.

435. Summary. As discussed above, the potential problems of leachates from the upland disposal of dredged material may come from contamination caused by TOC, alkalinity, manganese, iron, ammonia-nitrogen, nitrate-nitrogen, total lead, and possibly zinc. In general, pH, phosphorus, cadmium, copper, and mercury will not present serious contamination problems. However, it should be emphasized that the seriousness of contamination is usually dependent upon the eventual use of the impacted water, as well as the types of dredged material and soil in a particular upland disposal site. Also, dilution effects have been ignored in the above assessment.

Potential impact of dredged
material leachates

436. In previous discussions in this section of the report, existing water-quality criteria have been presented, compared to the experimental results and evaluated. As has been discussed, environmental problems caused by dredged material leachates are dependent on the types of dredged material and soils of a particular upland disposal site, as well as the eventual use of the impacted water. In addition to evaluating possible contaminating levels of constituents, it is desirable to ascertain relative mobilities, possible toxicities, and potential degree of hazard caused by various constituents in dredged material/leachates.

437. Three parameters are suggested for this examination as follows:

- Mobility Index (MI)
- Evaluatory Index (EI); and
- Impact Index (II).

438. Mobility Index. The Mobility Index (MI) will be defined as the ratio of the soluble concentration of certain constituents in the experimental dredged material interfacing soil leachates to that in the leachates prior to passage through the interfacing soils (i.e., interstitial water). This is illustrated as follows:

$$MI = \frac{\text{(concentration of soluble constituent in dredged material/interfacing soil leachates)}}{\text{(concentration of constituent in interstitial water of dredged material)}}$$

The MI value of any constituent can be used to evaluate the attenuative capacity for that constituent by an interfacing soil, when the constituent is in dredged material leachate. The higher the MI value the higher the amount of a constituent that will be released from a soil. An MI value of 1 means a constituent will pass through a particular soil virtually unchanged in concentration. An MI value of less than 1 means that a constituent is being attenuated by the soil.

439. The MI values for the constituents in this experiment are listed in Table 92; the values are based upon the average change in the leachate concentrations from the different types of dredged material (e.g., dredged material from Mobile, Sayerville, Grand Haven, and Seattle) after passage through each type of experimental soil. An understanding of attenuation capability of the two soil types for different constituents in dredged material leachates can be gained from this table. In comparing the two experimental soils (Lake Arrowhead sandy loam and Perkins loam), it can be seen that they have the relatively same MI values for TOC, ammonia-nitrogen, total Kjeldahl nitrogen (TKN), total phosphorus, cadmium, copper, and mercury. Perkins loam is seen to have relatively lower attenuative capacity for nitrate-nitrogen, orthophosphate, calcium, iron, and lead; and higher MI values were found for sodium, potassium, magnesium, and chloride. It should be emphasized that all the calculated MI values were based on the experimental leaching period of six months. Due to the time limitation of the experiment, the effect of longer leaching periods will not be covered in this discussion.

440. To compare the mobility of the various dredged material constituents, their relative mobility was ranked (Table 94); the results in this table were derived from the average value for the two soils as shown in Table 92. From Table 93, it can be seen that manganese, nitrate-nitrogen, total phosphorus, and iron were strongly released from the soil ($MI \geq 10$). Calcium, orthophosphate, TOC, zinc, chloride, total Kjeldahl nitrogen, potassium, mercury, and magnesium were found to be moderately released ($1 < MI < 10$). Copper, sodium, ammonia-nitrogen, lead, and cadmium were attenuated ($MI < 1$) by the soils in this experiment.

441. Evaluatory Index. To definitively evaluate the concentration of constituents in dredged material leachates

in relation to existing water quality standards, a comparison with EPA drinking water standards was developed. This comparison (the Evaluatory Index) (EI) is defined by the following equation:

$$EI = \frac{(\text{soluble concentration of constituent in dredged material/interfacing soil leachate})}{(\text{concentration of constituent in EPA drinking water standard})}$$

Since dilution is not being considered, EI values can give a "worst case" concept of the potential impact of a constituent based on the criteria developed for drinking water. The maximum allowable values of some constituents have not been established by EPA; therefore, this discussion will cover only the constituents for which criteria are available.

442. The EI values of constituents in different types of soils are presented in Table 93. The leachates from columns containing Perkins loam have higher EI values than the Lake Arrowhead sandy loam columns for the following constituents: ammonia-nitrogen, nitrate-nitrogen, total phosphorus, copper, and mercury. However, the EI values of orthophosphate, chloride, cadmium, iron, lead, manganese, and zinc are higher in the leachates from columns containing Lake Arrowhead sandy loam.

443. The EI rankings are listed in Table 94. As may be seen, the rankings of constituents are in the following order: Mn > TKN > Fe > Total P > Cl > NH₃-N > Pb > NO₃-N > Hg > Ortho-P > Cd > Zn > Cu. The EI of constituents below nitrate-nitrogen is less than 1 based on experimental results, indicating that these parameters will probably not cause problems when dredged material leachates discharge into a receiving water for a public water supply.

444. Impact Index. The MI and EI concepts presented provide one means for describing the relative mobility or

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impact of a constituent monitored during the experiment. In reality, the extent of environmental impact will not be based on the MI or EI indices alone; it will be determined by the potential aesthetic and toxicity effects of a constituent. An Impact Index (II) has been developed to aid in evaluating the potential impact of dredged material leachates on the environment. The Impact Index is the product of the Mobility Index and the Evaluatory Index for a particular constituent within the experimental period:

$$II = (MI) \times (EI)$$

445. The results for II are listed in Tables 93 and 94; constituents are ranked in terms of what would be expected from an overview of the experimental data. This ranking system provides a relative ranking of each constituent's expected impact on groundwater and surface waters. It also focuses attention on the constituents with the highest contamination potential, for which a reasonable remedy can be achieved.

446. In Table 93 it may be seen that manganese, iron, and total phosphorus had extremely high II values. Total Kjeldahl nitrogen, nitrate-nitrogen, and chloride also may potentially cause environmental problems. In general, environmental impact caused by orthophosphate, ammonia-nitrogen, mercury, lead, zinc, cadmium, and copper would be negligible based on the simulated dredged material/interfacing soil-leaching fluid systems studied.

Control of Groundwater Contamination from the Disposal of Dredged Material in Upland Areas

447. When dredged material is disposed on land, depending upon specific site conditions and physical and chemical characteristics of the dredged material being disposed,

resulting leachates have the potential for contaminating surface or groundwater supplies. Prevention of water supply contamination from dredged material disposal, then, may be of prime importance.

448. The prevention of groundwater contamination from leachates is not a new problem. Sanitary landfill designers and operators have been addressing this problem for many years; in general, liners or underdrain systems have been used to control leachates. Dredged material is somewhat different, however, because of its high initial moisture content and potential to form its own impermeable lining. Most municipal solid wastes develop leachates slowly as the disposed material becomes saturated. Dredged material can produce leachates immediately upon disposal because of its water content.

449. Despite the characteristics of dredged material leachates, they do not necessarily cause a serious threat. Many types of dredged material contain fine silty material which may form an impermeable lining as the materials settle (137). If the nearest water supply is far from the disposal site, the dredged material may seal the disposal site before enough leachate has been produced to threaten groundwater supplies. The need for a liner, then, becomes a function of dredged material and site characteristics.

450. Fine-grained dredged material is the most desirable if self-sealing properties are sought. In general, maintenance material and estuarine dredged material are finer grained than new work or littoral zone dredged material (138). Most of the materials studied in this project ranged from 50 to 100 percent silt and clay, giving permeabilities on the order of 10^{-6} to 10^{-7} cm/sec. Haxo studied silty dredged material from Napa River, California, and found permeabilities from 10^{-7} to 10^{-8} cm/sec (139). Materials this fine in texture have a potential use as liner materials for other types of waste disposal. Using dredged

material as a liner would require preliminary dewatering, however, presumably in a typical disposal-type lagoon setting. The original question of leachate from dredged material disposal sites remains.

451. Even with fine-grained dredged material, the sealing is not immediate. The fine particles necessary for filling soil pores and forming the impermeable layer remain in suspension longest and ultimately settle to the bottom (through gravity thickening). Thus, there is a period when the dredged material can form leachates fairly freely. Consequently, even fine-grained dredged material may require at least short-term liners, especially in areas where contamination of potable water supplies is a distinct possibility (as in high water table areas). For coarse-grained materials, a liner may be a necessity.

Liners

452. A potential disposal site with a high water table or nearby downstream surface water supply probably would require a liner, particularly if the dredged material leachate contains any hazardous contaminants or if the local soils are coarse and well drained. A fractured bedrock underlying the site is another indication of the need for a liner, while a site with a deep and/or fast-moving aquifer or underlain by a natural clay layer may need no further liner, especially if the dredged material is relatively innocuous. However, as discussed before, the natural clay layer may not be efficient enough to control the movement of anions, such as the chloride ion.

453. The type of liner appropriate for a given dredged material disposal site is a function of dredged material characteristics, costs, and site factors. In general, the liners can be broken down into several basic types: concrete, asphaltics, synthetics, membranes, clays, and soil

sealants. None of these materials is universally applicable, and all are susceptible to some contaminants which may be present in dredged material.

454. Costs have not been included in this discussion. For a proper cost comparison, a model site would have to be described, and all liner materials priced for that site. Because of local variations in materials and labor costs, materials availability, maintenance requirements and costs, and disposal site size, none of these estimates would necessarily be applicable for a given site, and the relative costs could change drastically.

455. Among other factors which must be considered when deciding on a liner are the ultimate use of the site, the possible use of heavy equipment to condition the dredged material, the presence or absence of vegetation near the site, the population of burrowing animals near the site, whether or how much the liner will be exposed to the environment, etc.

456. Table 95 lists major liner types with their primary characteristics. Permeabilities are usually expressed in centimeters/second; a permeability of 10^{-5} cm/sec represents water movement of about 1 cm/day. The best liners have permeabilities of no more than about 10^{-7} cm/sec. The permeabilities of synthetic membranes are recorded in perms ($\text{g}/24 \text{ hr}/\text{m}^2/\text{mm Hg}$).

457. Liner life is dependent upon the environmental conditions and the materials with which the liner is in contact. Since lagoon and landfill liners are mostly unexposed to environmental conditions, dredged material leachates become the main factor in determining liner life. The chemical constituents of the dredged material leachates can attack certain liner types and either degrade them entirely or seriously shorten their effective lifetimes. An obvious example is the degradation of asphaltics or

rubbers by oily materials or the chemical breakdown of clays by high salt solutions.

458. Short-lived liners are not necessarily useless; under certain conditions they can be just as safe and more economical than more permanent liners. For instance, given a fine-grained dredged material and a disposal site with a deep aquifer, the dredged material will seal the site in a relatively short time, and only temporary groundwater protection may be needed.

459. Table 96 shows the applicability of the various liners to different site and dredged material conditions. Since the descriptions are necessarily brief and general, each proposed disposal site and dredged material should be subjected to a thorough engineering analysis before a liner is chosen. Since suitability of existing natural clay layers is a site characteristic, clay layers are not included as liners in this table, but are incorporated into the site descriptions.

460. High silt dredged material is listed in both tables. Because of its low permeability, it has been proposed as a possible liner for the land disposal of other types of wastes. Haxo has even evaluated its liner capabilities for retaining hazardous leachates and sludges (139). It is included here for comparison.

Underdrain systems

461. Underdrains have been used for many years for the drainage of agricultural fields, building foundations, and engineering construction sites, and, more recently, for the collection and removal of landfill and other refuse disposal site leachates. In these applications, their purpose is to remove saturated soil-water conditions, lower water tables, reduce hydrostatic uplift (or buoyancy) pressures, and prevent the generation and production of landfill leachates.

462. The construction of an underdrain system presumes the following conditions:

- A saturated or very wet soil condition, and
- Permeable or slightly permeable soils that are amenable to drainage practices.

463. When a very permeable, porous subsoil is used for dredged material disposal, there is generally no need for an underdrain system if protection of a groundwater supply is not a consideration. Conversely, when the underlying soil is of a highly impermeable natural material such as clay, or overlain by a man-made impermeable liner (of a variety of materials), the water combined with the dredged material will need to be removed in some manner. Where confined by an impermeable barrier, the mechanism of dewatering is one of gravity settling and thickening with accompanying compressional thickening and dewatering. The water is gradually forced upward to the surface dredged material horizon, where it either evaporates, is decanted, or overflows from the lagoon.

464. As mentioned above, however, the majority of dredged material is of an impermeable or highly impermeable nature. Thus, maximum utilization of any underdrain system would occur during the initial filling of the upland disposal area, and its subsequent utility and effectiveness would incrementally decrease as the dredged material consolidated and compacted.

465. A relatively coarse and free-draining dredged material placed in an upland area would not need a system of underdrains since a simple slope of the area to a side or central collection sump where the water could be removed would be much more cost-effective. Since most dredged material is comprised of fine silt and/or clay which could conceivably blind the sand or gravel bed used to encase the underdrainage system, a very careful selection of sand or gravel packing around the underdrain

system is necessary (based on the characteristics of the dredged material to be placed). To select too coarse a sand and gravel packing would allow dredged material to completely silt-in the drainage pipes; conversely, too fine a material would result in severe blinding or clogging.

466. The construction of an underdrain system is time-consuming and an additional cost. As has been pointed out, the relative effectiveness of an underdrain system is expected to decrease with time, as successive layers of sediment build up around and over the underdrain system. Based on the permeability of the dredged material, few instances can be found where an underdrain system would be a cost-effective method for dewatering dredged slurry materials. Rather, an operation which is intended to protect the underlying groundwater, through appropriate site selection procedures based on soil characteristics or the installation of an impermeable liner, should rely on gravity thickening and settling with adequate provision for decanting of the surface liquids which accumulate.

Treatment of dredged material leachate

467. Previous landfill leachate treatability studies have indicated that variability of quality is one of the most difficult aspects in the treatment of leachate (154, 155, 156). Many factors contribute to this reported variability:

- Site operation and management
- Quantities and types of material disposed
- Site suitability
- Site hydrogeology
- Climate
- Season, and
- Site age.

Treatment systems perform optimally when hydraulic and pollutant loadings are constant. Thus, the inherent variability of leachate quality poses problems.

468. The feasibility of three basic techniques for treating dredged material leachate will be discussed in

this section: recirculation, biological treatment, and physical/chemical processes. To date, there has been virtually no research specifically addressing dredged material leachates in this area. As a result, many of the conclusions drawn in this section of the report rely heavily upon past research and experience with landfill leachates.

469. Recirculation. Recirculation is a technique that has been utilized in the past for treating sanitary landfill leachates. These systems trap and collect the leachate at the bottom of the fill with impermeable liners, sumps, and/or underdrains, and then pump it back to the top of the fill. This action hastens refuse decomposition. The recycled leachate provides moisture and nutrients for accelerated biological activity and further elutriation of chemical constituents, a process facilitated by the high permeability of most landfills: leachate percolates through the fill. In addition to enhanced decomposition, contaminants in the leachate are also removed by the filtering action of the fill. Recirculation is relatively inexpensive and easy to operate and maintain.

470. Unfortunately, recirculation appears to be ill-suited for most dredged material disposal sites because of the generally low permeability of materials contained in the sites. As reported by Jin et al., the average permeability of untreated dredged material tended to decrease significantly as time progressed after dredged material disposal on land (157). This may be due to: (1) the compressional thickening of the sediment and associated reduction in pore sizes, or (2) the clogging of drainage paths by eroded fines. The authors also noted that when the dredged material was treated with 1 percent lime (by weight of solids), a more open and stable structure was formed; permeability increased tenfold; more organics were removed in the leaching process; and long-term settlement was

increased (157). However, it is apparent that the permeabilities of most types of dredged material are not sufficient for recirculation treatment alone to be an effective treatment mode for dredged material leachates.

471. Biological treatment. In recent years, considerable research has been conducted on the biological treatment of leachate from sanitary landfills. Landfill leachate is typically characterized by high loadings of COD, nutrients, metals, and solids (Tables 97-98).

472. Boyle and Ham (154), and others, have shown that the leachates are amenable to both aerobic and anaerobic biological treatment. Removals of over 90 percent BOD, COD, and some metals have been reported. High concentrations of metals did not impair aerobic digestion as reported by Uloth and Mavinic (158). As can be seen in Table 99, all metals except potassium, lead, and magnesium were reduced more than 90 percent following gravity settling.

473. Although dredged material leachate may also be high in metals, it is usually low in BOD. Table 92 summarizes leachate qualities from the experiment under discussion. As shown, TOC levels averaged around 400 mg/l. However, much of this organic matter is stable and resists degradation. Typically, the easily degraded organics are broken down in the anaerobic sediment environment before dredging. Therefore, biological treatment does not appear to be optimal for dredged material leachate. Several problems that may develop with biological treatment are:

- Marginal treatability due to a low food to microorganism (F/M) ratio
- The tendency of organics in dredged material leachates to be refractory rather than easily biodegradable, thus limiting treatment performance; and
- The potential presence of high metal concentrations and toxic contaminants that may impede biological activity.

In summary, although biological treatment is a feasible treatment alternative for landfill leachate, it would not appear to be effective for treatment of dredged material leachate.

474. Physical/chemical treatment. Physical/chemical treatment offers the most promise for reducing contaminant concentrations in leachate from upland dredged material disposal areas. The characteristics of these leachates that favor physical/chemical treatment are the same as those mentioned previously:

- Low, stable organic loadings
- High metals and certain other contaminant concentrations associated with the solids fraction
- The potential presence of pesticides, herbicides, and exotic elements; and
- High solids concentrations.

475. In one of the few studies on chemical treatment of landfill leachates, Ho et al. investigated the effectiveness of various chemicals for precipitation, coagulation, and oxidation (156). Although the tests were performed on landfill leachate, the results presumably will be similar for dredged material leachate. The conclusions were:

- Of the two chemicals tested (lime and sodium sulfide), better chemical precipitation results were obtained with lime.
- Iron and other multivalent metals and color removals were virtually complete at high chemical doses (1,000 mg/l). However, there was no significant COD removal, and a large amount of sludge was produced.
- Both alum and ferric chloride were tested as chemical coagulants. The results were not very encouraging; both chemicals produced good removal of iron and color and little removal of COD, solids, etc. Further, high chemical doses were required, and large sludge volumes were produced.
- Four chemical oxidants were studied: chlorine, calcium hypochlorite, potassium permanganate, and ozone. In general, the results were good compared

with those for the precipitation and coagulation processes. Significant COD reductions were obtained with each oxidant, but high chemical doses were necessary. Excellent iron and color removals were obtained in all cases. Among the four oxidants tested, calcium hypochlorite was found the most promising, as it provided good removals and produced little sludge.

476. Thornton and Blanc also found chemical coagulation and precipitation effective in treating landfill leachate (159). Of the chemicals they tested, lime produced the best results. A substantial reduction of certain leachate contaminants, such as color, suspended solids, and multivalent cations, can be achieved using lime treatment. However, significant removals of other dissolved solids and the soluble organics, which account for the major portion of the BOD, were not observed. Large amounts of chemicals are required with lime dosages in the 300 to 600 mg/l range. Optimum chemical dosage varied with leachate strength. The removal of suspended solids, color, and multivalent cations is a function of the alkalinity of the sample and the ability of lime to raise the pH to favor the precipitation of calcium carbonate and metal hydroxides. Thus, the higher the acidity of a leachate, the greater the required lime dosage to accomplish a given degree of removal.

477. In a theoretical physical/chemical leachate treatment system, raw leachate from a dredged material disposal site is collected by the liner and transported to a wet well. From this point the leachate is pumped to a small, aerated blending pond where possible variations in flow and characteristics can be equalized. Aeration will develop an aerobic environment to avoid odor problems. Theoretically, little treatment will occur at this stage, except perhaps for the oxidation and removal of some metals (i.e., iron).

478. From the blending pond the leachate can be pumped to a solids contact upflow clarifier. The leachate

enters the chemical mix/coagulation inner tank where a heavy lime dosage is added with polymer to enhance floc formation. Upflow clarification follows, and the treated effluent is discharged. Sludge from the clarification stage can be dried in beds or with vacuum filters. Past experience has shown that removals of 90 percent can be achieved for most metals.

479. It should be emphasized at this point that this discussion is based purely on literature data and engineering assumptions. No known bench-scale tests have been performed on dredged material leachate to confirm the recommendation of physical/chemical treatment or determine contaminant removal capabilities of the various treatment techniques.

PART V: SUMMARY AND CONCLUSIONS

Introduction

480. Results of this experiment show that the migration of constituents in dredged material/interfacing soil systems is a complex phenomenon in which no single mechanism can account for all the trends and levels of constituent migration. There is no general rule or definitive model for explaining or predicting the migration of constituents that can properly reflect the characteristics of the dredged material, interfacing soils, and environmental conditions.

481. This part of the report will be divided into four sections:

- Mobilization of constituents in dredged material,
- Mobilization of constituents by interfacing soils
- Controlling mechanisms, and
- Impact of dredged material leachates on water quality.

The discussion on controlling mechanisms will apply to both the mobilization of constituents in dredged material and the subsequent mobilization of constituents by interfacing soils.

Mobilization of Constituents in Dredged Material

482. Throughout the experiment, pH values in the interstitial water of the dredged material approached levels of 8 from original values of approximately 6.7. Eh values measured in the upper few centimeters of the dredged material profile gradually increased throughout the leaching test; higher values were found to exist in the relatively coarse-grained dredged material. TOC levels were found to increase from about 100 ppm in the beginning to 300 to 600 ppm at the end of the experiment. Alkalinity levels also increased

slightly during the leaching test. Saline dredged material had higher final alkalinity levels (1,200 to 1,800 ppm as calcium carbonate) than the freshwater dredged material (400 to 600 ppm as calcium carbonate).

483. The concentrations of ammonia-nitrogen and total Kjeldahl nitrogen in the interstitial waters were found to be decreased after leaching. The final levels ranged from 0.1 to 15 ppm and 8 to 23 ppm, respectively, depending upon the type of dredged material. Both orthophosphate and total phosphorus levels were quite low in the interstitial waters; the levels of orthophosphate phosphorus were usually less than 0.01 ppm.

484. Throughout the experiment, sodium and potassium decreased in the interstitial waters; the levels that decreased correlated relatively well to the dilution ratio afforded by the passing of leaching fluid through the dredged material. Calcium too decreased throughout the course of the leaching test. Magnesium levels were relatively unchanged during the experiment. However, in the longer leaching of Columns 5 and 9, a decreasing trend of magnesium was noted in the freshwater dredged material. With one exception (Column 8), chloride levels gradually decreased throughout the leaching experiment.

485. In the interstitial waters of the dredged material, soluble iron concentrations in the saline and freshwater dredged material were in the range of 0.2 to 1.3 ppm and nil to 0.6 ppm, respectively. Manganese levels were observed to be in the same concentration ranges as iron; however, an increasing trend for manganese was observed. The migration trends of cadmium show an increase-decrease phenomenon; some columns had a second increase-decrease trend. The values of cadmium were in the ranges of 1 to 640 ppb for saline dredged material and nil to 3 ppb for freshwater dredged material. Soluble copper levels decreased from 10

to 70 ppb to less than 3 ppb during the leaching test. The mercury concentrations were usually less than 1 ppb. Final lead levels for saline dredged material increased to the range of 250 to 300 ppb. However, for freshwater dredged material the values decreased from 30 ppb to less than 1 ppb. Zinc was found to either decrease or suddenly increase and then decrease again throughout the course of the experiment; final levels were in the range of 1 to 120 ppb. Saline dredged material had higher zinc levels than freshwater. Chlorinated hydrocarbons were found to be strongly associated with dredged material; consequently, little release of chlorinated hydrocarbons from dredged material was found with usually nondetectable quantities present.

Mobilization of Constituents by Interfacing Soils

486. After leaching fluids passed through the interfacing soils in the experiment, the pH of the leaching fluids was gradually regulated by the soils. For Lake Arrowhead sandy loam, the final pH in the leachates was about 6.9; for Perkins loam, it was about 7.7. The TOC levels in leaching fluids were either unaffected or increased after they passed through the interfacing soils. Alkalinity levels in the leachates were decreased by Lake Arrowhead soil (final levels of about 350 to 500 ppm). Throughout the course of the experiment, the alkalinity levels in the Perkins loam were quite high initially (about 1,300 ppm), with either a resultant increase or decrease of alkalinity in the leachates after passage through the soil.

487. In the leachates, ammonia-nitrogen values were decreased by the soils in the initial experimental period; however, ammonia-nitrogen seemed to be slightly released after an extended period of time. Total Kjeldahl nitrogen usually increased in the leachates after passage through soil; the concentration could reach as high as 20 to 80 ppm,

depending upon the soil and dredged material. Phosphorus levels in leachates were usually very low. Orthophosphate concentrations were usually less than 0.1 ppm. Total phosphorus might be higher than 1 ppm, but was usually less than 0.1 ppm also.

488. When the leachates passed through the soils, attenuation of sodium by soil usually occurred. For leaching fluids high in sodium, the attenuation capacity of soil gradually decreased, as leaching time progressed. Potassium was found to be eluted from soils; the final soluble levels of potassium in leachates from freshwater dredged material were close to 20 ppm. In leachates from saline dredged materials, it was in the range of 50 to 160 ppm, depending upon the leaching media. Calcium was strongly released from the soils by the leaching solutions. The rate of release was higher in saline dredged material leachates than that in freshwater dredged material leachates. The final soluble calcium levels were 120 to 180 ppm and 450 to 2,300 ppm for freshwater and saline leachates, respectively. Magnesium was strongly attenuated by soil; the attenuative capacity decreased as the experimental period increased. Either attenuation or elution of chloride by the interfacing soils could occur, depending upon the relative levels of chloride in the leaching fluids and in the original soils.

489. The elution of iron in the leachates passing through the soils was very significant. Levels of soluble iron eluted ranged in concentration from 0.2 to 40 ppm, depending upon the dredged material and interfacing soil. The elution of manganese from soils was also very strong; the final soluble levels for Lake Arrowhead sandy loam leachates ranged from 20 to 120 ppm and from 1 to 18 ppm for Perkins loam leachates.

490. In general, soluble cadmium, copper, and lead were removed by soil. The final soluble cadmium in leachates

originating from freshwater and saline dredged material were decreased to nil and 1 to 20 ppb, respectively. Final soluble copper was usually less than 5 ppb, final soluble lead usually in the range of nil to 60 ppb. The exception was the Seattle dredged material which could cause high levels of lead in the leachates (as high as 450 ppb). Soluble mercury (usually less than 1 ppb) was found to be not much different in the influents and effluents of the interfacing soils; the particulate form of mercury, however, was found to be released (usually in the range of 5 to 30 ppb). The elution of zinc usually occurred in the experimental interfacing soils; the final soluble levels were in the range of 25 to 240 ppb, depending upon dredged material and interfacing soil. The migration of chlorinated hydrocarbons from interfacing soils was negligible.

Controlling Mechanisms

491. In this study, the major mechanisms which could affect the migration of constituents in dredged material/interfacing soil systems were solubilization, adsorption, complexation, redox reactions, ion exchange, and dilution.

492. It was found that solubilization could change the levels of calcium, magnesium, pH, alkalinity, and phosphorus, as well as all the trace metals in the interstitial waters of dredged material. Calcium, pH, and alkalinity levels were, for the most part, regulated by calcite. Soluble phosphorus was controlled principally by calcium phosphate solids. It was found that magnesium levels were probably affected by the minerals nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) and/or dolomite ($\text{CaMg}(\text{CO}_3)_2$). The solubility controlling solids for trace metals were gradually changed from reducing solids to more oxidizing solids throughout the course of the experiment. For example, the controlling solid for iron probably changed from sulfide solids to ferric hydroxide

solids or goethite between the beginning and end of experimentation. For manganese, the controlling solids probably changed from sulfide or carbonate solids to oxyhydroxide solids. However, if the solubility of oxidizing solids of trace metals is higher than the solubilities controlled by adsorption, the controlling mechanism for trace metal levels in the interstitial waters might change from solubilization to adsorption.

493. Adsorption could help account for the low levels of trace metals and chlorinated hydrocarbons in the interstitial waters of dredged material. The most important adsorbents were the hydrated oxides of iron and manganese, organic matter, and various clay minerals.

494. The complexation effect usually accounted for the high levels of trace metals in the interstitial waters of dredged material. The major ligands for complexation were chloride, carbonate, borate, hydroxide, and organic species.

495. In the interstitial waters of the dredged material, redox reactions were very important for the transformation of metal solids and various nitrogen compounds. Ion exchange probably could affect the transport of chloride species in interstitial waters, while dilution would become important when other reaction rates were relatively slow. Dilution was related to the flow rate of the leaching solution and the pore volume of the dredged material. This effect usually can decrease the concentrations of sodium, potassium, magnesium, and chloride in the interstitial waters of dredged material.

496. In the soil solution system the attenuation of soluble constituents by the experimental interfacing soils was usually governed by adsorption, precipitation, and ion exchange. However, the elution of soluble constituents was usually regulated by dissolution, complexation,

desorption, hydrolytic action, ion exchange, and bioconversion reactions. Physical scouring was the principal controlling mechanism for the release of particulate forms of the constituents from the soil.

497. The adsorption mechanism in the soil solution system was very important for the removal of ammonia-nitrogen, cadmium, copper, mercury, and lead from the leaching fluid by the interfacing soil. The major adsorbents were hydrated oxides of iron and manganese, clay minerals, and insoluble complex organic matter.

498. In the soil solution system, precipitation could attenuate phosphorus and some trace metals, as well as control the levels of hydrogen ion and alkalinity. The dissolution of metallic solids would become significant when there were solid transformations. In general, if the solubility of trace metals in the soil solution were controlled by solubilization, after passing through the soil, iron and manganese levels could be increased due to the formation of high solubility, low oxidation state solids. Similarly, if controlled by solubilization, the soluble levels of other trace metals usually could be decreased after long periods of leaching due to the formation of relatively lower solubility solids.

499. When there were high levels of trace metals in the soil solution system, complexation was probably responsible. Major complexation agents were organic matter, chloride, and carbonate species. Bioconversion and hydrolytic reactions were the major controlling mechanisms for the migration of organic matter and nitrogen compounds in soil solutions.

500. In this experiment, it was found that in both dredged material and interfacing soils there were large sinks and/or sources which readily controlled the environmental conditions of fluids that passed through them. Effects caused by varying leaching fluids, therefore, were

usually negligible. The effects on the migration of TOC, alkalinity, and calcium were the exception. Alkalinity and calcium in the leachates could be affected by the pH of the various leaching fluids used in Phase II of this study. TOC could be affected by the high input of organic matter to the dredged material/interfacing soil system.

Impact of Dredged Material Leachates on Water Quality

501. In comparing the experimental results of the constituents in the dredged material leachates from the lysimeter columns to the existing EPA, NAS, and NTAC water-quality standards, as well as related criteria from various state agencies, it was found that the potential impact on water quality is a function of the chemical composition and physical characteristics of the dredged material and interfacing soils and the planned use for the receiving waters. The analysis did not incorporate any site-specific factors such as potential dilution effects, climatic variations, etc. In general, pH, orthophosphate, cadmium, copper, mercury, and soluble lead should not present serious water-quality problems. However, the levels of ammonia-nitrogen, nitrate-nitrogen, alkalinity, iron, manganese, total lead, and possibly zinc, in the dredged material leachates might exceed either public water supply, freshwater (aquatic life), agriculture water, marine water (aquatic life), or groundwater criteria. In certain cases, protection of groundwaters prior to the disposal of dredged material to upland areas may be necessary. This protection may take the form of leachate collection through installation of clay or synthetic material barriers or underdrain systems. Leachate collected should be treated by recirculation, biological, or chemical methods prior to discharge. Although no bench-scale tests were performed, it is felt that chemical treatment may be the preferred method.

502. Based on a Mobility Index (MI) developed in this study, manganese, nitrate-nitrogen, total phosphorus, and iron were strongly released from the dredged material/interfacing soil systems ($MI \geq 10$) in comparison to levels in the dredged material interstitial water. Orthophosphate, zinc, chloride, total Kjeldahl nitrogen, potassium, and mercury were found to be moderately released ($1 < MI < 10$). Only copper, ammonia-nitrogen, lead, and cadmium were strongly attenuated by the interfacing soils ($MI \leq 1$). Considering EPA drinking water standards and the Mobility Index, it was found that the potential impact ranking of constituents in dredged material leachates is: manganese > iron > total phosphorus > total Kjeldahl nitrogen > nitrate-nitrogen > chloride > orthophosphate > ammonia-nitrogen > mercury > lead > zinc > cadmium > copper. The constituents preceding orthophosphate in the above ranking have Impact Indexes (II) higher than 1. This means that potential contamination problems might occur after the disposal of dredged material in an upland site overlying groundwaters used for drinking purposes. However, it should be emphasized that this ranking is based upon the described experimental leaching period and the specific dredged material and soils used and ignores dilution, and thus it can only be used as a guide to the potential for impact.

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Table 1
Theoretical Redox Conditions for Redox Couples

| Redox Couple | Reaction | Eh (mV) | |
|---|--|---------|------|
| | | pH=7 | pH=8 |
| $\text{Fe}^{3+} - \text{Fe}^{2+}$ | $\text{Fe}^{3+} + e = \text{Fe}^{2+}$ | +764 | +764 |
| $\text{NO}_3^- - \text{N}_2(\text{g})$ | $1/5 \text{NO}_3^- + 6/5 \text{H}^+ + e = 1/10 \text{N}_2(\text{g}) + 3/5 \text{H}_2\text{O}$ | +759 | +687 |
| $\text{MnO}_2(\text{s}) - \text{MnOOH}(\text{s})$ | $\text{MnO}_2(\text{s}) + \text{H}^+ + e = \text{MnOOH}(\text{s})$ | +670 | +610 |
| $\text{Mn}_3\text{O}_4(\text{s}) - \text{MnCO}_3(\text{s})$ | $1/2 \text{Mn}_3\text{O}_4(\text{s}) + 3/2 \text{HCO}_3^-(10^{-2}) + 5/2 \text{H}^+ + e = 3/2 \text{MnCO}_3(\text{s}) + 2\text{H}_2\text{O}$ | +610 | +460 |
| $\text{MnO}_2(\text{s}) - \text{MnCO}_3(\text{s})$ | $1/2 \text{MnO}_2(\text{s}) + 1/2 \text{HCO}_3^-(10^{-2}) + 3/2 \text{H}^+ + e = 1/2 \text{MnCO}_3(\text{s}) + 3/8 \text{H}_2\text{O}$ | +570 | +480 |
| $\text{MnOOH}(\text{s}) - \text{MnCO}_3(\text{s})$ | $\text{MnOOH}(\text{s}) + \text{HCO}_3^-(10^{-2}) + 2\text{H}^+ + e = \text{MnCO}_3(\text{s}) + 2\text{H}_2\text{O}$ | +550 | +430 |
| $\text{MnOOH}(\text{s}) - \text{Mn}_3\text{O}_4(\text{s})$ | $3\text{MnOOH}(\text{s}) + \text{H}^+ + e = \text{Mn}_3\text{O}_4(\text{s}) + 2\text{H}_2\text{O}$ | +440 | +380 |
| $\text{NO}_3^- - \text{NO}_2^-$ | $1/2 \text{NO}_3^- + \text{H}^+ + e = 1/2 \text{NO}_2^- + 1/2 \text{H}_2\text{O}$ | +429 | +369 |
| $\text{MnOOH}(\text{s}) - \text{MnS}(\text{s})$ | $\text{MnOOH}(\text{s}) + \text{HS}^-(3 \times 10^{-6}) + 2\text{H}^+ + e = \text{MnS}(\text{s}) + 2\text{H}_2\text{O}$ | +407 | +287 |
| $\text{NO}_3^- - \text{NH}_4^+$ | $1/8 \text{NO}_3^- + 5/4 \text{H}^+ + e = 1/8 \text{NH}_4^+ + 3/8 \text{H}_2\text{O}$ | +369 | +294 |
| $\text{NO}_2^- - \text{NH}_4^+$ | $1/6 \text{NO}_2^- + 4/3 \text{H}^+ + e = 1/6 \text{NH}_4^+ + 1/3 \text{H}_2\text{O}$ | +349 | +268 |

(Continued)

Table 1

(Concluded)

| Redox Couple | Reaction | Eh (mV) | |
|---|---|---------|------|
| | | pH=7 | pH=8 |
| $\text{FeOOH(s)} - \text{FeS(s)}$ | $\text{FeOOH(s)} + \text{HS}^-(3 \times 10^{-6}) + 2\text{H}^+ + \text{e}$ $= \text{FeS(s)} + 2\text{H}_2\text{O}$ | -34 | -154 |
| $\text{FeOOH(s)} - \text{FeCO}_3(\text{s})$ | $\text{FeOOH(s)} + \text{HCO}_3^-(10^{-2}) + 2\text{H}^+ + \text{e}$ $= \text{FeCO}_3(\text{s}) + 2\text{H}_2\text{O}$ | -40 | -160 |
| $\text{SO}_4^{2-} - \text{S}^0(\text{s})$ | $1/6 \text{SO}_4^{2-} + 4/3 \text{H}^+ + \text{e} = 1/6 \text{S}^0(\text{s}) + 2/3 \text{H}_2\text{O}$ | -198 | -278 |
| $\text{SO}_4^{2-} - \text{H}_2\text{S(g)}$ | $1/8 \text{SO}_4^{2-} + 5/4 \text{H}^+ + \text{e} = 1/8 \text{H}_2\text{S(g)} + 1/2 \text{H}_2\text{O}$ | -210 | -255 |
| $\text{SO}_4^{2-} - \text{HS}^-$ | $1/8 \text{SO}_4^{2-} + 9/8 \text{H}^+ + \text{e} = 1/8 \text{HS}^- + 1/2 \text{H}_2\text{O}$ | -225 | -292 |
| $\text{S}^0(\text{s}) - \text{H}_2\text{S(g)}$ | $1/2 \text{S}^0(\text{s}) + \text{H}^+ + \text{e} = 1/2 \text{H}_2\text{S(g)}$ | -246 | -307 |
| $\text{CO}_2(\text{g}) - \text{CH}_4(\text{g})$ | $1/8 \text{CO}_2(\text{g}) + \text{H}^+ + \text{e} = 1/8 \text{CH}_4(\text{g}) + 1/4 \text{H}_2\text{O}$ | -247 | -308 |
| $\text{N}_2(\text{g}) - \text{NH}_4^+$ | $1/6 \text{N}_2(\text{g}) + 4/3 \text{H}^+ + \text{e} = 1/3 \text{NH}_4^+$ | -281 | -359 |
| $\text{Fe(OH)}_3(\text{s}) - \text{FeS(s)}$ | $\text{Fe(OH)}_3(\text{s}) + \text{HS}^-(3 \times 10^{-6}) + 2\text{H}^+ + \text{e}$ $= \text{FeS(s)} + 3\text{H}_2\text{O}$ | -327 | -447 |
| $\text{Fe(OH)}_3(\text{s}) - \text{FeCO}_3(\text{s})$ | $\text{Fe(OH)}_3(\text{s}) + \text{HCO}_3^-(10^{-2}) + 2\text{H}^+ + \text{e}$ $= \text{FeCO}_3(\text{s}) + 3\text{H}_2\text{O}$ | -385 | -504 |

Table 2
Common Natural Solid Species of Metals*

Cadmium

Oxide: CdO (monteporrite)

Hydroxide: Cd(OH)_2

Carbonate: CdCO_3 (otavite)

Sulfide: CdS (greenockite)

Calcium

Hydroxide: Ca(OH)_2

Carbonates: CaCO_3 (calcite); CaCO_3 (aragonite); $\text{CaMg(CO}_3)_2$ (dolomite)

Sulfide: CaS (oldhamite)

Sulfates: CaSO_4 ; CaSO_3

Phosphates: $\text{Ca}_2\text{P}_2\text{O}_7$; CaHPO_4 ; $\text{Ca}_3(\text{PO}_4)_2$; $\text{CaH}_2(\text{PO}_4)_2$;
 $\text{Ca}_5\text{OH(PO}_4)_3$; $\text{Ca}_4\text{H(PO}_4)_3$; $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$

Halides: CaF_2 ; CaBr_2 ; CaI_2

Silicates: $\text{NaCaFBe(SiO}_3)_2$ (leucophane); $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$ (laumontite); CaSiO_3 (wollastonite); $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ (diopside); $\text{Ca}_{10}\text{Mg}_2\text{Al}_4(\text{Si}_2\text{O}_7)_2(\text{SiO}_4)_5(\text{OH})_4$ (idocrase); $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite);
 $\text{Ca}_{0.33}\text{Al}_{4.67}\text{Si}_{2.33}\text{O}_{20}(\text{OH})_4$ (Ca - montmorillonite)

Copper

Native: Cu^0

Oxides: Cu_2O (cuprite); CuO (tenorite)

Hydroxides: $\text{CuCl}_2 \cdot 3\text{Cu(OH)}_2$ (atacamite); Cu(OH)_2

*Ref. 10.

(Continued)

Table 2

(Continued)

Copper (Continued)

Carbonates: $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (malachite); $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ (azurite); CuCO_3

Simple sulfides: Cu_2S (chalcocite); CuS (covellite)

Complex sulfides: CuFeS_2 (chalcopyrite); Cu_5FeS_4 (bornite); Cu_3AsS_4 (enargite); $(\text{Cu},\text{Fe})_{12}\text{Sb}_4\text{S}_{13}$ (tetrahedrite)

Sulfates: $\text{Cu}_4(\text{OH})_6\text{SO}_4$ (brochantite); $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (chalcantite)

Silicates: $\text{CuSiO}_3 \cdot n\text{H}_2\text{O}$ (chrysocolla); $\text{CuO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ (diopside)

Iron

Oxides: Fe_2O_3 (hematite); FeOOH (goethite); Fe_3O_4 (magnetite); $\text{FeOOH} \cdot n\text{H}_2\text{O}$ (limonite)

Hydroxides: $\text{Fe}(\text{OH})_3$; $\text{Fe}_3(\text{OH})_8$ (ferrosoferric hydroxide)

Carbonate: FeCO_3 (siderite)

Sulfides: FeS_2 (pyrite); Fe_{1-x}S (pyrrhotite); FeS (machinawite); Fe_3S_4 (greigite)

Sulfate: $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_4$ (jarosite)

Phosphate: FePO_4

Silicates: FeSiO_3 (glaucophane); $(\text{Fe(II)},\text{Fe(III)},\text{Mg},\text{Al})(\text{Si},\text{Al})_{0.7-3-5}(\text{OH})_{4-1}$ (chamosite)

Lead

Native: Pb^0

(Continued)

Table 2

(Continued)

Lead (Continued)

Oxides: PbO (massicot); PbO_2 (plattnerite); Pb_3O_4 (minium);
 PbCrO_4 (crocoite); PbMoO_4 (wulfenite)

Hydroxide: Pb(OH)_2

Carbonates: PbCO_3 (cerussite); $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ (hydrocerussite)

Sulfide: PbS (galena)

Sulfate: PbSO_4 (anglesite)

Chlorides: $3\text{Pb}_3\text{As}_2\text{O}_8 \cdot \text{PbCl}_2$ (mimetite); $3\text{Pb}_3\text{V}_2\text{O}_8 \cdot \text{PbCl}_2$
 (vanadinite)

Magnesium

Oxides: MgO (periclase); $\text{Mg}_7\text{Cl}_{12}\text{B}_{16}\text{O}_{30}$ (boracite); MgAl_2O_4
 (spinel)

Hydroxides: Mg(OH)_2 (brucite)

Carbonates: $\text{MgCa}(\text{CO}_3)_2$ (dolomite); MgCO_3 (magnesite); MgCO_3
 (nesquehonite); $3\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 3\text{H}_2\text{O}$ (hydromagnesite)

Sulfide: MgS

Sulfate: MgSO_4

Phosphates: $\text{MgNH}_4(\text{PO}_4)$; $\text{Mg}_3(\text{PO}_4)_2$; $\text{MgNH}_4(\text{PO}_4)(\text{H}_2\text{O})_6$;
 $\text{MgK}(\text{PO}_4)(\text{H}_2\text{O})_6$; $\text{MgHPO}_4(\text{H}_2\text{O})_3$

Halides: MgF_2 ; $\text{KMgCl}_3(\text{H}_2\text{O})_3$; $\text{MgCl}_2(\text{H}_2\text{O})_6$; MgCl_2

Silicates: MgSiO_3 (clinoenstatite); Mg_2SiO_4 (forsterite);
 $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (vermiculite); $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
 (talc)

(Continued)

Table 2

(Continued)

Manganese

Simple oxides: MnO_2 (pyrolusite); Mn_3O_4 (hausmannite);
 MnOOH or Mn_2O_3 (manganite); $\text{MnO}_{1.2}$ to MnO_2
 (non-stoichiometric oxides)

Complex oxides: $(\text{Mn},\text{Si})_2\text{O}_3$ (braunite); $\text{Mn}_3\text{O}_4 \cdot \text{Fe}_3\text{O}_4$
 (vrendenburgite); $(\text{Mn},\text{Fe})_2\text{O}_3$ (bixbyrite);
 $(\text{Mn(II)Fe})(\text{Mn(III)Fe})_2\text{O}_4$ (jacobsite);
 $\text{BaMn(II)Mn(IV)}_8\text{O}_{16}(\text{OH})_4$ (psilomelane)

Hydroxides: Mn(OH)_2 (pyrochroite); Mn(OH)_3

Carbonate: MnCO_3 (rhodochrosite)

Sulfide: MnS (alabandite)

Silicates: MnSiO_3 (rhodonite); $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$ (spessartite)

Mercury

Native: Hg^0

Oxides: HgO ; HgSb_4O_7 (livingstonite)

Hydroxide: Hg(OH)_2

Sulfide: HgS (cinnabar)

Sulfate: $\text{HgSO}_4 \cdot 2\text{HgO}$

Chlorides: HgCl_2 ; Hg_2OCl ; Hg_4OCl_2 ; Hg_2Cl_2 (calomel)

Potassium

Oxides: $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$ (carnotite)

Phosphates: $\text{K}_3\text{PO}_4(\text{MoO}_3)_{11}$; $\text{K}_3\text{PO}_4(\text{WO}_3)_{12}$

Halide: K_2SiF_6

(Continued)

Table 2

(Concluded)

Potassium (Continued)

Silicates: $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ (alunite); $\text{KAl}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ (muscovite); KAlSi_3O_8 (orthoclase); $\text{K}(\text{Mg,Fe})_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ (biotite)

Sodium

Oxides: Na_2VO_4 ; $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ (kramite);
 $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ (ullexite); $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

Sulfate: NaHSO_4

Halide: Na_2SiF_6

Silicates: $\text{NaAlSi}_3\text{O}_8$ (albite); Na-Montmorillonite;
 $\text{NaCaBeF}(\text{SiO}_3)_2$ (leucophane); $\text{Na}_2\text{Al}_2\text{SiO}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ (natrolite); $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ (jadeite);
 $\text{NaCa}_2(\text{Mg,Fe,Al})_5(\text{Si,Al})_8\text{O}_{22}(\text{OH})_2$ (hornblende)

Zinc

Oxide: ZnO (zincite)

Hydroxide: $\text{Zn}(\text{OH})_2$

Carbonate: ZnCO_3 (smithsonite)

Sulfide: ZnS (sphalerite)

Sulfate: $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (goslarite)

Silicate: ZnSiO_3 ; $2\text{ZnO} \cdot \text{SiO}_2$ (willemite); $\text{Zn}_2\text{SiO}_4 \cdot n\text{H}_2\text{O}$ (calamine); $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$ (hemimorphite)

Table 3
Important Solubility Products (K_{sp}) of Trace Metals*

| Metal | Oxide | Hydroxide | Carbonate | Sulfide | Chloride | Phosphate | Silicate |
|---------|-------------------------------------|---|---|-------------------------------------|--|--|---|
| Cd(II) | | 13.6 | 13.6 | 26.1 | | | |
| Ca(II) | | 5.26 | 8.32 (calcite), 8.22 (aragonite), 16.7 (dolomite) | 2.94 | | 6.25 (CaHPO_4) 26 ($\text{Ca}_3(\text{PO}_4)_2$) 1.14 ($\text{CaH}_2(\text{PO}_4)_2$) 6.4 ($\text{CaHPO}_4(\text{H}_2\text{O})_2$) 40.9 ($\text{Ca}_4\text{H}(\text{PO}_4)_3$) 44.6 ($\text{Ca}_5\text{OH}(\text{PO}_4)_3$) 120.8 ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) | 3.7 (CaSiO_3), 52.3** (anorthite), 585 (ca-montmorillonite) |
| Cu(II) | 20.4 | 18.6 | 9.63 (CuCO_3), 33.2 ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) | 35.2 | | 37.7 | |
| Fe(II) | | 15.3 | 10.2 | 16.9 (FeS) | | | 18.9** |
| Fe(III) | 80** (Fe_2O_3) | 39.3 | | 18.2 (Fe_3S_4) | | 25.8 | |
| Pb(II) | 15.4 (PbO) | 16.1 18.8 ($\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$) | 13.1 | 26.6 | 4.79 | 43.5, 12.6** (PbHPO_4) | |
| Mn(II) | | 9.2 (active), 11.6 (brucite) | 4.9 (magnesian site), 5.4 (nesquehonite), 16.7 ($\text{MgCa}(\text{CO}_3)_2$)** | | 4.44** (MgCl_2) (H_2O) ₆ , 4** (KMgCl_3) (H_2O) ₃ | 28.4 ($\text{Mg}_3(\text{PO}_4)_2$) 12.6** ($\text{Mg}_3\text{H}_4(\text{PO}_4)_3$) 13.2** ($\text{Mg}_3\text{H}_4\text{PO}_4(\text{H}_2\text{O})_6$) 5.0** ($\text{Mg}_2\text{HPO}_4(\text{H}_2\text{O})_3$) | |

(Continued)

Table 3

(Continued)

| Metal | Oxide | Hydroxide | Carbonate | Sulfide | Chloride | Phosphate | Silicate |
|--------|--------|--|-----------|--|----------|-----------|--|
| Mn(II) | 0.92** | 12.7 | 9.3 | 12.9 (crys- taline), 15.7 (precipi- tated) | | 22 | 13.2** |
| Hg(II) | 25.7** | 25.4 | | 52.2 (meta- cinnabar) 53.6 (cinnabar) | 13.8 | | |
| K(I) | | | -4.11 | | | | 76** (orthoclase) 124** (muscovite) |
| Na(I) | | | | | | | 40.6** (albite) 294** (Na-montmor- illonite) |
| Zn(II) | | 15.7 (Amor- phous), 16 (Amor- phous, aged), 16.9 (cryst. aged) | 10.8 | 25.2 (sphal- erite), 22.8 (wurzite), 22.1 (pre- cipitated) | | 36.7 | 21.03** |

(Continued)

Table 3

(Concluded)

*Values in pK_{sp} ($\log K_{sp}$) when I (ionic strength) = 0, T (temperature) = 25°C.

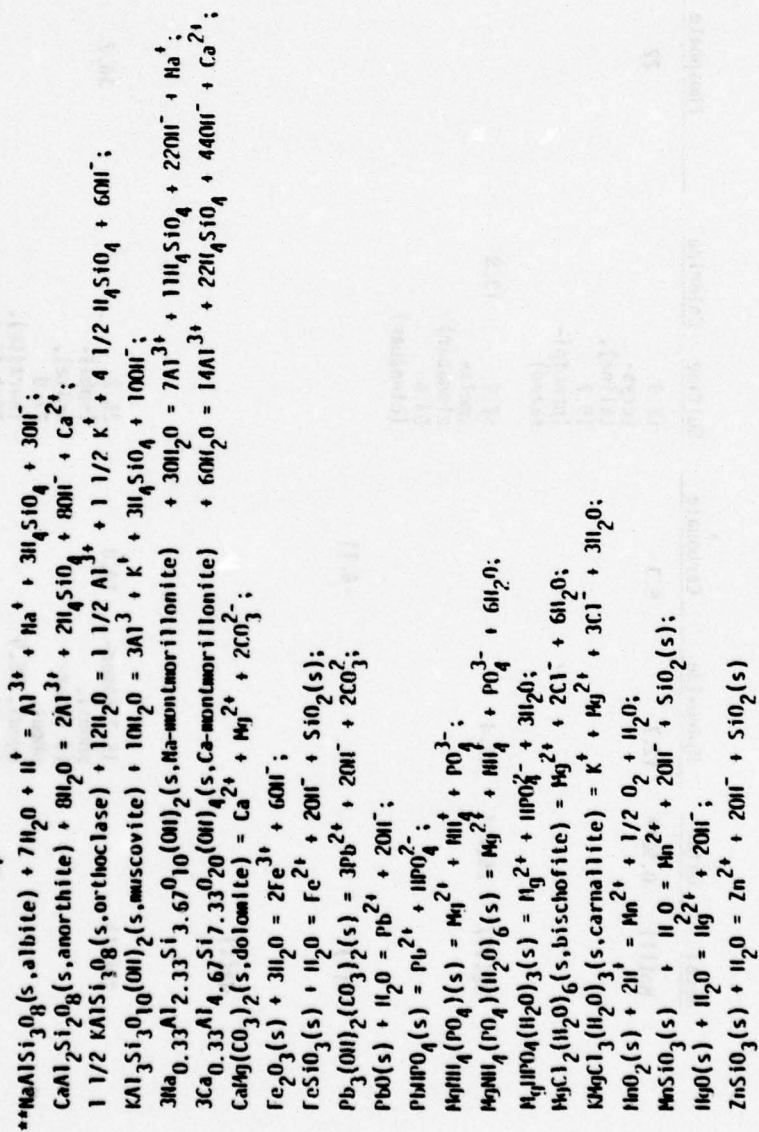


Table 4
Tension Plate Studies

| <u>Experimental Purpose</u> | <u>Environmental Variables</u> | <u>Design Limitations</u> | <u>Reference</u> |
|---|--------------------------------|--|------------------|
| Water movement on steep slopes | Ambient conditions | Little control over experimental conditions | 64 |
| Leachate-ion concentration of gravitational water | Ambient conditions | Limited to ambient conditions | 65 |
| Ion movement through soils | Grass cover and bare soil | Adapted for coarse soils | 66 |
| Permeability and sealing capacity of clay sealant | Wetting and drying cycles | Basically only a permeability measuring device | 67 |

Table 5
Studies on In Situ Lysimeter Columns

| <u>Experimental Purpose</u> | <u>Environmental Variables</u> | <u>Project Design Limitations</u> | <u>Reference</u> |
|----------------------------------|---|--|------------------|
| Evapotranspiration research | Ambient conditions | Only measures rainfall and evaporation | 68 |
| Water flow in soil | Irrigation and ambient conditions | Model of moisture movement limited to coarse soils | 69 |
| Salt accumulation in soil | Saltwater irrigation; natural rainfall kept out | Little environmental control | 70 |
| Nitrogen movement in soil | Weekly irrigation with distilled water | Large land usage required | 71 |
| Measurement of water percolation | Ambient conditions | Limited scope | 72 |
| Gas and leachate generation | Anaerobic leachate collection under argon gas | Large land usage required | 73 |

Table 6
Laboratory Soil Lysimeter Column Studies

| <u>Experimental Purpose</u> | <u>Environmental Variables</u> | <u>Design Limitations</u> | <u>Reference</u> |
|------------------------------------|---|---|------------------|
| Sludge constituent effect on soils | Tops of columns open to environment; body of columns under controlled temperature | Airborne pollutants not accounted for | 74 |
| Sanitary landfill simulator | Completely controlled | Too large to operate relatively inexpensively | 75 |
| Evaluating landfill liners | Completely controlled | No leachate collection system | 76 |
| Leachate attenuation of soils | Leachate addition to columns | Columns not saturated | 77 |
| Ion movement mechanisms | Evaporation minimized by plastic soil cover | No drain system; filter candles only | 78 |
| Denitrification soils | Gas and water introduction regulated | No drain system; filter candles only | 79 |
| Soil-water evaporation | Controlled evaporation | Limited parameter examination (only water movement studied) | 80 |

Table 7
Field Sampling Sites

| <u>Site Location</u> | <u>Reason for Selection</u> |
|---|--|
| Grand Haven, Michigan | Freshwater sediment source |
| Seattle, Washington | Contained high concentrations of polychlorinated biphenyls. Saline sediment source |
| Sayerville, New Jersey | Contained high concentrations of heavy metals. Brackish sediment source |
| Pinto Island, Alabama | Contained high concentrations of heavy metals. Brackish sediment source |
| Houston, Texas (Clinton disposal area) | Contained high concentrations of oil and grease. Brackish sediment source |

Table 8
Interfacing Soil Selection

| <u>Interfacing Soil</u> | <u>Reason for Selection</u> |
|--------------------------|--------------------------------|
| Perkins loam | Relatively low organic content |
| Lake Arrowhead silt loam | High organic content |

Table 9
Sampling Materials Required

-
- a. Adequate supply of 19-l (5-gal), hermetically sealing polyethylene buckets and lids
 - b. Corrugated shipping cartons (at least 75 x 45 x 45 cm (30 x 18 x 18 in.) lined around the inside with 1 cm (3/8 in.) of styrofoam and above the styrofoam with 6.5 mm (1/4 in.) of plywood
 - c. One box of heavy-duty (3-mil) trash can liners
 - d. One shovel, the shovel head edges lined with split garden hose
 - e. Sufficient prefrozen blue ice for shipping dredged material samples
 - f. Several rubber bands
 - g. Two meters (several feet) of baling wire
 - h. One pair of pliers
 - i. Pocket knife
 - j. Several rolls of fiber packing tape
 - k. Several black waterproof marking pens; and
 - l. Notebook for field work and calculations.
-

Table 10
Materials Introduced to Lysimeter Columns

| Column Number | Soil Type | Weight of Soil Added to Column (kg) | Dredged Material | Volume of Dredged Material Added to Column (ℓ) | Weight of Dredged Material Added to Column (kg) |
|---------------|---------------------------|-------------------------------------|------------------|--|---|
| 1 | Lake Arrowhead sandy loam | 12.2 | Mobile | 25.3 | 23.6 |
| 2 | Lake Arrowhead sandy loam | 11.5 | Sayerville | 27.2 | 23.8 |
| 3 | Lake Arrowhead sandy loam | 11.8 | Seattle | 20.9 | 24.0 |
| 4 | Lake Arrowhead sandy loam | 11.3 | Grand Haven | 23.0 | 27.2 |
| 5 | Lake Arrowhead sandy loam | 11.3 | Grand Haven | 19.0 | 23.0 |
| 6 | Perkins loam | 16.0 | Sayerville | 21.8 | 25.1 |
| 7* | Lake Arrowhead sandy loam | 11.3 | -- | -- | -- |
| 8 | Perkins loam | 15.9 | Seattle | 22.0 | 22.4 |
| 9 | Perkins loam | 15.6 | Grand Haven | 26.0 | 23.0 |
| 10* | Perkins loam | 15.6 | -- | -- | -- |
| 11 | Lake Arrowhead sandy loam | 12.5 | Houston | 26.4 | 22.9 |
| 12 | Perkins loam | 13.4 | Houston | 24.7 | 24.9 |
| 13 | Perkins loam | 14.6 | Houston | 23.2 | 24.2 |
| 14 | Perkins Loam | 15.2 | Houston | 25.8 | 23.7 |
| 15 | Perkins loam | 13.5 | Houston | 24.3 | 24.9 |
| 16 | Perkins loam | 13.9 | Houston | 25.2 | 25.0 |

*Soil control columns.

Table 11
Experimental Configuration - Phase I

| Column Number | Dredged Material | Interfacing Soil | Leaching Fluids | Periods of Operation (months) |
|---------------|------------------|---------------------------|--|-------------------------------|
| 1 | Mobile | Lake Arrowhead sandy loam | Ultrapure distilled water to simulate rain water | 6 |
| 2 | Sayerville | Lake Arrowhead sandy loam | Ultrapure distilled water to simulate rain water | 6 |
| 3 | Seattle | Lake Arrowhead sandy loam | Ultrapure distilled water to simulate rain water | 6 |
| 4 | Grand Haven | Lake Arrowhead sandy loam | Ultrapure distilled water to simulate rain water | 6 |
| 5 | Grand Haven | Lake Arrowhead sandy loam | Ultrapure distilled water to simulate rain water | 6 |
| 6 | Sayerville | Perkins loam | Ultrapure distilled water to simulate rain water | 6 |
| 7 | -- | Lake Arrowhead sandy loam | Ultrapure distilled water to simulate rain water | 6 |
| 8 | Seattle | Perkins loam | Ultrapure distilled water to simulate rain water | 6 |
| 9 | Grand Haven | Perkins loam | Ultrapure distilled water to simulate rain water | 6 |
| 10 | -- | Perkins loam | Ultrapure distilled water to simulate rain water | 6 |

Table 12

Experimental Configuration - Phase II

| <u>Column Number</u> | <u>Dredged Material</u> | <u>Interfacing Soil</u> | <u>Leaching Fluids</u> | <u>Periods of Operations (months)</u> |
|----------------------|-------------------------|---------------------------|--|---------------------------------------|
| 11 | Houston | Lake Arrowhead sandy loam | Ultrapure distilled water adjusted to pH 4.5 with SO ₂ gas to simulate acid rainfall | 3 |
| 12 | Houston | Perkins loam | Ultrapure distilled water adjusted to pH 4.5 with SO ₂ gas to simulate acid rainfall | 3 |
| 13 | Houston | Perkins loam | Leachate from municipal sanitary landfill | 3 |
| 14 | Houston | Perkins loam | 75 ppm fulvic acid in ultrapure distilled water | 3 |
| 15 | Houston | Perkins loam | 50 ppm as CaCO ₃ hardness and 50 ppm as CaCO ₃ alkalinity added to ultrapure distilled water to simulate groundwater | 3 |
| 16 | Houston | Perkins loam | Ultrapure distilled water adjusted to pH 4.5 with SO ₂ gas to simulate acid rainfall | 3 |

Table 13

Dredged Material/Soil Analyses

| <u>University of Southern California, Department of Environmental Engineering</u> | | <u>SCS Engineers</u> |
|---|--|--------------------------|
| Chloride (Cl^-) | | Cation Exchange Capacity |
| Chlorinated Pesticides | | Density |
| Interstitial Water Volume | | Exchangeable Cations |
| Moisture Content | | Grain Size Distribution |
| Ammonia Nitrogen ($\text{NH}_3\text{-N}$) | | Permeability |
| Kjeldahl Nitrogen | | |
| Nitrate-Nitrogen ($\text{NO}_3\text{-N}$) | | |
| Oil and Grease | | |
| Polychlorinated Biphenyls (PCB's) | | |
| Orthophosphate ($\text{PO}_4\text{-P}$) | | |
| Total Phosphorus | | |
| pH | | |
| Total Organic Carbon (TOC) | | |
| Total Sulfide (ΣS^-) | | |
| Cadmium (cd) | | |
| Calcium (Ca) | | |
| Copper (Cu) | | |
| Iron (Fe) | | |
| Lead (Pb) | | |
| Magnesium (Mg) | | |
| Manganese (Mn) | | |
| Mercury (Hg) | | |
| Potassium (K) | | |
| Sodium (Na) | | |
| Zinc (Zn) | | |

Table 14

Leachate Analysis

| University of Southern California, Department of Environmental Engineering | Weck Laboratories | | SCS Engineers |
|--|--|---------------------------------------|---------------|
| | | | |
| Cadmium (Cd) | Chlorinated Pesticides | Alkalinity | |
| Calcium (Ca) | Kjeldahl Nitrogen | Ammonia-Nitrogen (NH ₃ -N) | |
| Copper (Cu) | Nitrate-Nitrogen (NO ₃ ⁻ -N) | Chloride (Cl ⁻) | |
| Iron (Fe) | Oil and Grease | Conductivity | |
| Lead (Pb) | Polychlorinated Biphenyls (PCB's) | pH | |
| Magnesium (Mg) | Orthophosphate (PO ₄ -P) | | |
| Manganese (Mn) | Total Phosphorus | | |
| Mercury (Hg) | Total Organic Carbon (TOC) | | |
| Potassium (K) | Total Sulfide (ΣS ⁼) | | |
| Sodium (Na) | | | |
| Zinc (Zn) | | | |

Table 15
Analyses Performed

| <u>Total Leachate Fraction</u> | <u>Soluble Leachate Fraction</u> |
|---|---|
| Chloride (Cl^-) | Alkalinity |
| Chlorinated Pesticides | Chloride (Cl^-) |
| Kjeldahl Nitrogen | Conductivity |
| Oil and Grease | Ammonia-Nitrogen ($\text{NH}_3\text{-N}$) |
| Orthophosphate ($\text{PO}_4\text{-P}$) | Kjeldahl Nitrogen |
| Total Phosphorus | Nitrate-Nitrogen |
| Polychlorinated Biphenyls (PCB's) | Ammonia-Nitrogen ($\text{NH}_4\text{-N}$) |
| Total organic carbon (TOC) | Phosphate ($\text{PO}_4\text{-P}$) |
| Cadmium (Cd) | Total Phosphorus |
| Calcium (Ca) | pH |
| Copper (Cu) | Total Organic Carbon (TOC) |
| Iron (Fe) | Total Sulfides ($\Sigma\text{S}^{=}$) |
| Lead (Pb) | Cadmium (Cd) |
| Magnesium (Mg) | Calcium (Ca) |
| Manganese (Mn) | Copper (Cu) |
| Mercury (Hg) | Iron (Fe) |
| Potassium (K) | Lead (Pb) |
| Sodium (Na) | Magnesium (Mg) |
| Zinc (Zn) | Manganese (Mn) |
| | Mercury (Hg) |
| | Potassium (K) |
| | Sodium (Na) |
| | Zinc (Zn) |

Table 16
Physical Characteristics of Dredged Material
and Interfacing Soils

| Soil/Dredged Material | Particle-Size Distribution | | | Texture Type | Permeability cm/sec | Bulk Density g/ml |
|------------------------------|----------------------------|-------------|-------------|--------------------|------------------------|----------------------|
| | Sand (%) | Silt (%) | Clay (%) | | | |
| Lake Arrowhead Sandy Loam | 72.5 | 19.5 | 8 | sandy loam | 1.8×10^{-3} | 1.12 |
| Perkins Loam | 28 | 54.5 | 17.5 | silt loam | 7.9×10^{-5} | 1.33 |
| Mobile | 7.5 | 50.5 | 42 | silty clay | 2.8×10^{-6} | 0.97 |
| Sayerville | 32 | 50 | 18 | silt loam | 2.2×10^{-6} | 1.65 |
| Grand Haven | 50 | 30 | 20 | sandy clay loam | 8.9×10^{-5} | 1.16 |
| Seattle | 0 | 77 | 23 | silt loam | 6.2×10^{-6} | 0.98 |
| Houston | 6.5 | 44 | 49.5 | silty clay | 1.3×10^{-6} | 0.97 |

Table 17
Chemical Characterization of Dredged Material
and Interfacing Soils
(all concentrations in ppm (mg/kg) dry weight basis unless specified)

| Parameters | Lake Arrowhead Sandy Loam | Perkins Loam | Hobble | Sayerville | Grand Haven | Seattle | Houston |
|------------------------------|------------------------------|--------------|--------|------------|-------------|---------|---------|
| pH | 5.2 | 7.1 | 6.8 | 6.4 | 6.8 | 6.5 | 6.7 |
| CEC, meq/100 g | 35 | 25 | 37 | 14 | 23 | 23 | 32 |
| Moisture Content (%) | 28 | 19.4 | 45.8 | 35.2 | 38.5 | 52.8 | 40.4 |
| Solid Content (%) | 72 | 80.6 | 54.2 | 66.8 | 61.5 | 47.2 | 59.6 |
| TOC (%) | 1.95 | 0.55 | 1.21 | 2.82 | 4.77 | 3.10 | 1.48 |
| COD | 56,900 | 18,500 | 44,700 | 73,700 | 128,700 | 101,300 | 86,790 |
| Oil and Grease | 823 | 387 | 2,995 | 2,472 | 3,577 | 5,245 | 9,490 |
| NH ₃ -N | 14 | 33 | 206 | 110 | 146 | 163 | -- |
| Organic Nitrogen | 813 | 832 | 1,030 | 1,250 | 1,670 | 1,060 | 1,410 |
| Total Kjeldahl Nitrogen | 827 | 865 | 1,236 | 1,360 | 1,816 | 1,223 | 1,410 |
| Acid Soluble S ²⁻ | 12.6 | 13.2 | 1,090 | 1,550 | 1,170 | 3,070 | 657 |
| Orthophosphate-P | 4.3 | 11.3 | 26.0 | 15.8 | 6.9 | 13.0 | 18.4 |
| Total Phosphorus | 242 | 522 | 884 | 1,530 | 870 | 1,280 | 1,010 |
| Calcium | 3,700 | 3,730 | 658 | 1,500 | 17,000 | 11,200 | 7,380 |
| Chloride | 33 | 32 | 7,320 | 5,750 | 40 | 20,580 | 4,480 |
| Potassium | 31,100 | 17,550 | 17,300 | 23,100 | 22,900 | 24,300 | 12,300 |
| Sodium | 16,300 | 20,500 | 11,780 | 19,610 | 32,720 | 39,100 | 21,240 |
| Cadmium | 1.5 | 1.6 | 0.8 | 9.2 | 22.6 | 66.5 | 3.5 |
| Copper | 8.1 | 20.8 | 21.4 | 286.1 | 56.3 | 129.6 | 83.6 |
| Iron | 11,920 | 11,690 | 15,800 | 13,870 | 10,800 | 19,800 | 21,100 |
| Lead | 6.2 | 6.4 | 12.0 | 45.0 | 7.7 | 49.6 | 55.5 |
| Magnesium | 4,140 | 5,770 | 4,510 | 7,190 | 11,400 | 12,700 | 4,470 |
| Manganese | 426 | 548 | 528 | 334 | 443 | 498 | 235 |
| Mercury | 0.529 | 0.476 | 0.745 | 1.26 | 0.406 | 0.735 | 0.950 |
| Zinc | 64.4 | 66.1 | 207.7 | 285.5 | 158.3 | 444.8 | 433 |

Table 18
Concentrations of Exchangeable Cations in Dredged Material
and Interfacing Soils
 (all units in ppm)

| | <u>Cd</u> | <u>Cu</u> | <u>Fe</u> | <u>Hg</u> | <u>Mn</u> | <u>Pb</u> | <u>Zn</u> | <u>Na</u> | <u>K</u> | <u>Ca</u> | <u>Mg</u> |
|----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|-----------|-----------|
| Lake Arrowhead | 0.05 | 0.08 | | 0.04 | 7.2 | 0.3 | 12.4 | 4,800 | 70 | 2,800 | 80 |
| Perkins | 0.066 | 0.12 | 0.5 | 0.06 | 16 | 0.26 | 6.4 | 3,560 | 98 | 4,000 | 120 |
| Mobile | 0.06 | 0.02 | 0.2 | 0.04 | 35 | 0.24 | 4.0 | 3,400 | 8,400 | 3,000 | 860 |
| Sayerville | 0.05 | 0.16 | 0.4 | 0.08 | 9.4 | 0.22 | 4.6 | 2,580 | 820 | 4,700 | 620 |
| Grand Haven | 0.05 | 0.18 | 0.4 | 0.06 | 42 | 0.22 | 13.6 | 100 | 86 | 5,700 | 300 |
| Seattle | 0.058 | 0.04 | 0.4 | 0.04 | 12 | 0.32 | 4.4 | 3,840 | 1,960 | 5,100 | 2,160 |
| Houston | 0.05 | 0.17 | 0.4 | 0.07 | 18 | 0.27 | 6.7 | 2,760 | 1,500 | 5,220 | 1,840 |

Table 19
Chlorinated Hydrocarbons* in Dredged Material
and Interfacing Soils
(all units in ppb)

| | o,p'DDE | o,p'DDD | o,p'DDT | p,p'DDE | p,p'DDD | p,p'DDT | Total DDT | PCB 1242 | PCB 1254 | PCB 1260 | Total PCB's |
|-------------------|---------|---------|---------|---------|---------|---------|-----------|-------------|-------------|-------------|----------------|
| Lake Arrowhead | - | - | - | 1 | - | 47 | 48 | - | - | - | - |
| Perkins | - | - | 10 | 1 | - | 22 | 33 | - | 15 | 1.6 | 16.6 |
| Mobile | 14 | 9 | 94 | 8 | 41 | 341 | 507 | - | 65 | 6.5 | 71.5 |
| Sayerville | - | 27 | 58 | - | 14 | - | 99 | 437 | 408 | 40 | 885 |
| Grand Haven | - | 16 | - | 5 | 12 | 71 | 104 | - | 83 | 8 | - |
| Seattle | - | 120 | - | - | - | - | 120 | 184,600 | 2,310 | 231 | 187,141 |
| Houston | 600 | 40 | 60 | 1,000 | 70 | 70 | 1,840 | 260 | 160 | 16 | 436 |

*Heptachlor, aldrin, endrin, and dieldrin are all below detection limits. Dash indicates below detection limit.

Table 20
Analysis of Municipal Sanitary Landfill Leachate*

| <u>Parameter</u> | <u>Concentration</u> |
|--|----------------------|
| TOC | 280 |
| Total Kjeldahl Nitrogen | 504 |
| Nitrate Nitrogen - $\text{NO}_3\text{-N}$ | 0.30 |
| Total Phosphorus | 1.43 |
| Orthophosphate - $\text{PO}_4\text{-P}$ | 0.94 |
| Oil and Grease | 23.5 |
| Calcium (Ca) | 228 |
| Magnesium (Mg) | 151 |
| Potassium (K) | 295 |
| Sodium (Na) | 455 |
| Cadmium (Cd) | 0.0003 |
| Copper (Cu) | 0.003 |
| Iron (Fe) | 4.7 |
| Lead (Pb) | 0.0005 |
| Manganese (Mn) | 27.3 |
| Mercury (Hg) | 0.002 |
| Zinc (Zn) | 14.7 |
| Chlorinated Pesticides (ppb as Tetrachloroethane) | 0.45 |
| Polychlorinated Biphenyls (ppb as Arochlor 1248) | N.D.** |

*All values in parts per million unless otherwise stated.
 **Not detectable.

Table 21
Migration and Attenuation of pH in Simulating Dredged Material
Disposal to Upland Areas - Phase I

| Column Number | Dredged Material / Interfacing Soil | Sample Type | Sampling Date | | | | | | |
|---------------|--------------------------------------|-------------------------|---------------|--------|---------|---------|---------|---------|---------|
| | | | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction | | 5.84 | 7.13 | | 7.16 | 7.03 | 6.97 |
| | | Interstitial Water | | 8.88 | | | | | |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction | | 6.70 | 6.87 | 7.98 | 6.77 | 6.80 | 6.83 |
| | | Interstitial Water | | 8.95 | 8.54 | | | 8.57 | |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction | | 6.01 | 6.39 | 7.66 | 6.61 | 6.87 | |
| | | Interstitial Water | | 8.32 | 8.17 | 8.02 | | 8.20 | |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction | | 6.72 | 7.17 | 8.36 | 7.20 | 7.13 | 7.20 |
| | | Interstitial Water | | 7.24 | 7.42 | | 7.75 | 7.80 | 7.75 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction | 5.95 | 6.99 | 6.26 | 8.06 | 6.86 | 6.77 | 6.83 |
| | | Interstitial Water | | 7.42 | 7.01 | | 7.55 | 7.68 | 7.73 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction | | 7.25 | 7.37 | 8.12 | 7.79 | 7.79 | 7.63 |
| | | Interstitial Water | | 8.36 | 8.64 | 7.96 | | 8.26 | |
| 7 | -/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction | | | 5.88 | 6.80 | | 6.38 | 6.36 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction | | 7.85 | 7.61 | 7.35 | 7.50 | 7.70 | |
| | | Interstitial Water | | 8.27 | 7.27 | | | 8.11 | |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction | 8.45 | 6.77 | 7.97 | 7.80 | 7.32 | 7.87 | 7.80 |
| | | Interstitial Water | | 8.00 | 7.23 | | 8.00 | 7.96 | 8.07 |
| 10 | /Perkins Loam (Soil Blank Column) | Total Leachate Fraction | | | 7.55 | 7.58 | 7.56 | 7.56 | 7.55 |

Table 22
Migration and Attenuation of Total Organic Carbon in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/ Interfacing Soil | Sample Type | Sampling Date | | | | | | | |
|---------------|---|--|---------------|-------------------|-------------------|-------------------|---------|-------------------|------------|-----------|
| | | | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 | |
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 170 | 390 | | | 430 720 | 280 | 320 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 160 240 | 195 220 | 420 | | 480 | 340 330 | 195 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 99 130 136 | 350 156 390 | 800 | | 550 720 | 930 170 | |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 100 290 | 97 350 | 230 | | 650 320 560 | 240 39 | 320 80 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 120 | 140 | 650 430 | | 660 510 580 | 320 28 | 320 30 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 70 380 | 64 354 380 | 900 | | 770 | 350 370 | 420 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | 150 | 230 | 390 | | 900 | 800 | 310 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 365 370 130 | 335 390 210 | 670 600 300 | | 730 710 | | |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 210 | 475 405 85 | 330 300 77 | 240 | | 250 310 | 220 21 | 95 110 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 111 250 | 270 | | 230 240 | 175 | 92 |

Table 23
Migration and Attenuation of Alkalinity in Simulating Dredged Materials
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
|---------------|---------------------------------------|--|--------|-----------------------|-------------------------|---------------------|-----------------------|----------------|--------------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 208 | | | 239 239 | 250 | 280 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 125 42 1,100 | 394 332 1,061 | | 208 208 | 330 1,530 | 370 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 42 913 | 104 581 | 1,868 1,286 | 373 245 | 280 1,188 | |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 187 581 | 291 581 | 291 332 | 518 709 | 384 609 | 412 590 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 374 | 145 332 | 62 519 | 550 560 | 559 682 | 298 546 | 339 540 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 1,296 1,224 | 1,245 1,453 1,183 | 923 1,826 | 691 641 | 1,170 1,534 | 1,200 |
| 7 | --/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 540 187 | 312 | | 439 | 508 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 1,100 1,245 955 | 1,245 1,038 1,328 | 519 540 1,598 | 395 395 | 890 1,268 | |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 830 | 1,245 1,245 415 | 913 955 208 | 1,639 550 | 1,840 1,840 423 | 1,294 460 | 1,324 480 |
| 10 | --/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 1,058 875 | 1,142 | 1,377 1,050 | 1,280 | 1,288 |

Table 24
Alkalinity Constituents in the Final Dredged Material Leachate*

| Column Number | pH | Alkalinity (meq/L) | $[\text{NH}_3](\text{M})$ | $C_T(\text{M})$ | $[\text{HCO}_3^-](\text{M})$ |
|---------------|-----|--------------------|---------------------------|-----------------------|------------------------------|
| 2 | 8.5 | 30 | 4.8×10^{-4} | 2.9×10^{-2} | 2.8×10^{-2} |
| 3 | 8.2 | 24 | 7×10^{-6} | 2.35×10^{-2} | 2.3×10^{-2} |
| 4 | 7.8 | 11.8 | 4×10^{-4} | 1.1×10^{-2} | 1.1×10^{-2} |
| 5 | 7.7 | 10.8 | 7×10^{-6} | 1.05×10^{-2} | 1×10^{-2} |
| 6 | 8.2 | 30 | 1×10^{-4} | 2.95×10^{-2} | 2.9×10^{-2} |
| 8 | 8.1 | 24 | 4×10^{-4} | 2.3×10^{-2} | 2.27×10^{-2} |
| 9 | 8.1 | 8.1 | 5×10^{-4} | 9×10^{-3} | 8.89×10^{-3} |

*Assume borate concentrations are equal to $4.5 \times 10^{-4}\text{M}$.

Table 25
Migration and Attenuation of Organic Nitrogen in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/ Interfacing Soil | Sample Type | Sampling Date | | | | | | | |
|---------------|---|--|---------------|------------------------|-----------------------|---------|-------------|----------------------|--------------|--------------|
| | | | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 | |
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 10.3 | 23.5 | | | 42.7 | 51.0 | 54.6 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 8.71 | 11.26 | | 11.6 | 38.9 | 27.7 | 60.7 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 15.62 12.49 12.2 | 36.25 | | 38.0 | 18.7 | 16.9 | |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 5.94 | 27.3 | | | 18.7 | 3.41 | 23.9 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 18.29 | 47.7 14.09 | 79.1 13.7 | | 37.5 | 5.5 | 43.9 | 40.3 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 20.6 32.88 41.2 | 31.65 | | 22.8 | 8.5 | 14.6 39.5 | 67.6 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | | .35 | | 3.8 3.16 | | | |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 34.12 27.20 | 37.07 | | | 75.7 | 1.2 | |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 19.5 | 19.22 23.30 12.5 | 26.0 45.4 16.53 | | | 16.8 25.2 14.3 | 8.6 16.1 | 23.9 29.8 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | | | | | | | |

Table 26
Migration and Attenuation of Ammonia (as NH₃) in Simulating Dredged
Material Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | Sampling Date | | | | | | |
|---------------|---------------------------------------|--|---------------|---------------|---------------|---------|---------|---------|---------|
| | | | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.10 19.70 | 2.21 | | 1.26 | 0.96 | 1.39 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.39 28.22 | 2.84 34.00 | 7.65 | 2.30 | 2.40 | 3.31 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 4.98 11.22 | 5.95 1.53 | 4.42 | 4.42 | 6.72 | |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.36 19.04 | 6.54 13.60 | 5.61 | 11.56 | 8.39 | 7.56 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.81 | 0.61 11.52 | 0.30 13.60 | 0.04 | 2.12 | 4.77 | 5.57 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 4.42 49.30 | 5.95 49.30 | 12.58 | 0.04 | 0.83 | 1.88 |
| 7 | --/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | 1.36 | 0.85 | 7.56 | 0.04 | 0.08 | 0.13 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 4.08 10.54 | 6.63 6.12 | | 0.04 | 4.92 | 3.88 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 1.70 | 5.78 28.39 | 4.76 28.05 | 1.26 | 1.95 | 15.46 | 1.12 |
| 10 | --/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 6.97 | | 0.05 | 0.96 | |
| | | | | | | | | 6.88 | |
| | | | | | | | | 5.79 | |
| | | | | | | | | 3.38 | 5.49 |
| | | | | | | | | 6.36 | 7.06 |
| | | | | | | | | 0.63 | 0.89 |

Table 27
Migration and Attenuation of Total Kjeldahl Nitrogen in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
|---------------|--------------------------------------|--|--------|----------------------|----------------------|----------------------|----------------------|---------|--------------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 10.4 | 25.7 | | 44.0 32.6 | 52 | 56 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 9.1 | 14.1 21.7 | 19.2 | 41.2 36.0 | 30.1 | 54 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 19.7 18.1 23.4 | 42.2 44.2 | 42.4 | 23.1 48.4 | 12.1 | |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 6.3 | 33.8 23.9 | 9.3 | 30.3 20.6 | 11.8 | 31.5 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 11.0 | 66.7 | 92.7 | 28.1 43.1 | 7.6 | | |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 14.7 | 14.0 15.6 | 34.6 22.8 | 29.7 29.3 9.8 | 44.7 | 42.2 19.8 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | 32.1 | 37.6 41.9 | 44.6 98.9 | 49.3 | 19.5 | 71.5 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 90.51 | 1.2 1.98 | 4.4 | 17.1 | 40.5 | 28.5 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 21.2 | 38.2 30.6 | 43.7 50.4 42.3 | 80.9 74.3 21.7 | 83.3 75.7 | 8.1 | |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 25 25 40.9 | 30.8 28.2 29.9 | 40.0 14.8 | 18.7 37.0 23.1 | 12.0 | 29.4 |
| | | Total Leachate Fraction Soluble Leachate Fraction | | | 23.5 17.8 | 24.7 | 14.3 18.4 | 16.7 | 30.7 |

Table 28
Migration and Attenuation of Nitrate-Nitrogen in Simulating Dredged
Material Disposal to Upland Areas - Phase I
(all values in ppm)

(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | Sampling Date | | | | | | |
|---------------|---|--|---------------|------------------------|----------------|---------|---------|---------------|---------------|
| | | | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.05 | | | 0.05 | 0.28 | 0.30 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | <0.01 | 0.17 | | 0.03 | 0.26 | 0.26 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.035 0.014 0.15 | 0.02 0.08 | 0.042 | <0.01 | 0.17 0.04 | |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | <0.01 0.48 | 0.02 | | 0.06 | 19.3 19.17 | 30.38 30.0 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | <0.01 | <0.01 | 0.01 | | 0.04 | 2.28 | 1.08 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.345 <0.01 | <0.01 0.135 | <0.01 | | 0.17 33.7 | 0.33 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | | <0.01 0.42 | 0.025 | | 0.26 | 0.36 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | <0.06 <0.02 | <0.02 0.15 | <0.01 | | 0.40 | |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.06 | <0.01 <0.02 0.05 | 0.05 | | 1.12 | 3.70 | 3.06 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 0.13 0.015 | <0.01 | 0.81 | 3.10 | 2.38 |

Table 29
Migration and Attenuation of Total Phosphorus in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
|---------------|---------------------------------------|--|--------|-----------------------|----------------------|-------------------------|-------------------------|--------------|--------------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.10 0.58 | 0.17 | | 0.09 0.06 | 0.06 | 0.04 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.065 | 0.12 0.09 | <0.01 | 0.013 0.06 | 0.04 | 0.05 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.08 0.035 2.9 | 0.09 | <0.01 | 0.23 <0.01 | 0.12 | |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.11 0.62 0.03 | 6.75 0.60 0.02 | 2.13 0.02 0.16 | <0.01 <0.01 0.012 | 0.26 0.4 | 0.21 0.3 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.16 | 0.16 | 0.2 0.06 0.01 | <0.01 <0.01 0.043 | <0.01 <0.01 0.043 | 0.04 1.62 | 0.11 0.41 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.15 | 0.36 2.1 0.25 | 0.15 0.013 | <0.01 | 0.07 2.12 | 0.11 |
| 7 | --/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | 0.09 | 0.25 0.34 | 0.25 | <0.01 | 0.29 | 0.11 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.26 0.04 1.14 | 0.24 0.36 0.24 | <0.01 <0.01 3.6 | 0.01 <0.01 | 0.09 | |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.36 | 0.14 0.04 <0.01 | 0.26 0.24 0.02 | 0.28 0.02 | 0.08 <0.01 <0.01 | 0.16 | 0.21 1.50 |
| 10 | --/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 0.89 0.11 | 0.46 | 0.01 <0.01 | 0.21 | 0.30 |

Table 30
Migration and Attenuation of Phosphate in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/ Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
|---------------|--|--|--------|------------------------|--------------------------|-------------------------|-------------------------|---------|--------------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.048 | 0.05 | | <0.01 <0.01 | 0.06 | 0.03 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.05 0.315 | 0.025 0.015 NA | | <0.01 <0.01 | 0.02 | 0.03 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.04 0.02 0.635 | 0.06 0.02 4.5 | <0.01 <0.01 0.115 | <0.01 <0.01 | 0.03 | |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.03 0.093 | 0.163 0.05 0.019 | <0.01 <0.01 <0.01 | <0.01 <0.01 | 0.06 | 0.05 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.124 | 0.05 <0.01 | 0.038 <0.025 <0.01 | <0.01 <0.01 <0.01 | <0.01 <0.01 <0.01 | 0.03 | 0.05 0.40 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.025 <0.025 | 0.34 0.02 0.075 | <0.01 <0.01 <0.01 | <0.01 | 0.06 | 0.08 |
| 7 | --/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 0.10 0.038 | | <0.01 | 0.07 | 0.10 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.255 0.02 0.05 | 0.21 0.043 0.023 | <0.01 <0.01 0.017 | <0.01 <0.01 | 0.04 | |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.31 | 0.04 0.015 <0.01 | 0.075 0.038 <0.01 | | <0.01 <0.01 <0.01 | 0.03 | 0.07 |
| 10 | --/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 0.50 0.02 | | 0.033 <0.01 | 0.07 | 0.14 |

Table 31
Stability Calculations of Phosphorus Species

Assuming apatite was the controlling solid:

$$[PO_4^{3-}] = \left(\frac{10^{-55} [H^+]}{10^{-14} [Ca^{2+}]^5} \right)^{1/3} = \frac{10^{-13.7} [H^+]^{1/3}}{[Ca^{2+}]^{5/3}} \quad (20)$$

Total orthophosphate concentration =

$$P_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \quad (21)$$

+ metal- PO_4 complexes

$$= [PO_4^{3-}] \left[\frac{[H^+]^3}{6.3 \times 10^{-22}} + \frac{[H^+]^2}{10^{-19}} + \frac{[H^+]}{10^{-12}} + 1 \right] \quad (22)$$

$$= 1.1 \times 10^4 [PO_4^{3-}]$$

$$P_T = \frac{1.1 \times 10^4 \times 10^{-13.7} [H^+]^{1/3}}{[Ca^{2+}]^{5/3}} = \frac{10^{-9.66} [H^+]^{1/3}}{[Ca^{2+}]^{5/3}} \quad (23)$$

Experimental results show that pH = 8

and $[Ca^{2+}]$ to be 1.5×10^{-3} - 3.6×10^{-3} M (60-220 ppm)

$$P_T = 5.51 \times 10^{-9} \sim 2.37 \times 10^{-8} \text{ M} \quad (24)$$

$$= 0.0002 \sim 0.0007 \text{ ppm}$$

Assuming variscite was the controlling solid:

$$[PO_4^{3-}] = \frac{10^{-21}}{[Al^{3+}]} \quad (25)$$

Total aluminum concentration =

$$Al_T = [Al^{3+}] + [Al(OH)_4^-] \quad (26)$$

$$= [Al^{3+}] \left[1 + \frac{[OH^-]^4}{10^{-35}} \right]$$

$$= 10^4 [Al^{3+}]$$

Assuming Al_T in the interstitial water

$$= 3.7 \times 10^{-7} \sim 3.7 \times 10^{-6} \text{ M}$$

$$\therefore [Al^{3+}] = 3.7 \times 10^{-18} \sim 3.7 \times 10^{-17} \text{ M} \quad (27)$$

$$\therefore P_T = \frac{1.1 \times 10^4 \times 10^{-21}}{[Al^{3+}]} \quad (28)$$

$$= 2.97 \times 10^{-1} \sim 2.97 \text{ M}$$

$$= 9.2 \times 10^3 \sim 9.2 \times 10^4 \text{ ppm}$$

Table 32
Migration and Attenuation of Sodium in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
|---------------|--------------------------------------|---------------------------|--------|--------|---------|---------|---------|---------|---------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction | 24 | 22 | | 22 | 360 | 404 | 636 |
| | | Soluble Leachate Fraction | 22 | | | 22 | 355 | 353 | 606 |
| | | Interstitial Water | | | | 3,900 | 3,425 | | |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction | 25 | 25 | | 114 | 818 | 606 | 909 |
| | | Soluble Leachate Fraction | 22 | 22 | | 113 | 811 | 555 | 576 |
| | | Interstitial Water | 6,000 | 6,000 | | 5,350 | 3,465 | 3,180 | 3,080 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction | 1,848 | 1,848 | | 6,000 | 6,237 | 5,600 | 5,680 |
| | | Soluble Leachate Fraction | 1,800 | 1,800 | | 5,650 | 6,215 | 5,600 | 5,150 |
| | | Interstitial Water | 7,780 | 7,780 | | 5,950 | 4,642 | 4,340 | 4,470 |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction | 25 | 25 | | 8 | 26 | 17 | 21 |
| | | Soluble Leachate Fraction | 24 | 24 | | 7 | 17 | 15 | 20 |
| | | Interstitial Water | 82 | 82 | | 55 | 38 | 54 | 56 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction | 20 | 23 | | 9 | 24 | 14 | 21 |
| | | Soluble Leachate Fraction | 23 | 23 | | 8 | 19 | 12 | 20 |
| | | Interstitial Water | 70 | 70 | | 52 | 38 | 31 | 42 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction | 180 | 180 | | 154 | 225 | 263 | 606 |
| | | Soluble Leachate Fraction | 180 | 180 | | 153 | 220 | 348 | 505 |
| | | Interstitial Water | 6,320 | 6,320 | | 5,880 | 4,455 | 3,430 | 3,640 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction | | | | 12 | 14 | 9 | 8 |
| | | Soluble Leachate Fraction | | | | 9 | 12 | 8 | 7 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction | 216 | 216 | | 650 | 1,628 | 3,340 | 2,720 |
| | | Soluble Leachate Fraction | 181 | 181 | | 600 | 1,540 | 3,230 | 2,420 |
| | | Interstitial Water | 8,800 | 8,800 | | 8,000 | 7,150 | 6,160 | 7,200 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction | 216 | 192 | | 157 | 116 | 132 | 157 |
| | | Soluble Leachate Fraction | 208 | 208 | | 151 | 107 | 84 | 93 |
| | | Interstitial Water | 79 | 79 | | 58 | 31 | 30 | 31 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction | | | | 177 | 134 | 210 | 216 |
| | | Soluble Leachate Fraction | | | | 167 | 125 | 144 | 172 |

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Table 33
Migration and Attenuation of Potassium in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
|---------------|--------------------------------------|---------------------------|--------|--------|---------|---------|---------|---------|---------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction | | 26 | | 500 | 85 | 58 | 85 |
| | | Soluble Leachate Fraction | | 25 | | 205 | 82 | 56 | 73 |
| | | Interstitial Water | | | | 115 | 161 | | |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction | | 21 | | 475 | 90 | 67 | 86 |
| | | Soluble Leachate Fraction | | 20 | | 310 | 90 | 63 | 84 |
| | | Interstitial Water | | 421 | | 210 | 185 | 176 | 176 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction | | 400 | | 1,070 | 182 | 162 | 152 |
| | | Soluble Leachate Fraction | | 390 | | 970 | 177 | 162 | 152 |
| | | Interstitial Water | | 542 | | 180 | 429 | 218 | 215 |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction | | 26 | | 260 | 49 | 23 | 25 |
| | | Soluble Leachate Fraction | | 23 | | 130 | 48 | 23 | 24 |
| | | Interstitial Water | | 33 | | 125 | 14 | 12 | 8 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction | 24 | 30 | | 390 | 52 | 23 | 24 |
| | | Soluble Leachate Fraction | | 25 | | 170 | 50 | 22 | 24 |
| | | Interstitial Water | | 27 | | 165 | 15 | 5 | 8 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction | | 233 | | 195 | 75 | 53 | 65 |
| | | Soluble Leachate Fraction | | 160 | | 55 | 73 | 53 | 63 |
| | | Interstitial Water | | 432 | | 241 | 396 | 202 | 197 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction | | | | 220 | 39 | 21 | 21 |
| | | Soluble Leachate Fraction | | | | 85 | 37 | 18 | 20 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction | | 235 | | 970 | 129 | 96 | 107 |
| | | Soluble Leachate Fraction | | 168 | | 805 | 126 | 61 | 106 |
| | | Interstitial Water | | 590 | | 260 | 550 | 293 | 293 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction | 165 | 241 | | 460 | 53 | 25 | 27 |
| | | Soluble Leachate Fraction | | 157 | | 320 | 51 | 24 | 27 |
| | | Interstitial Water | | 32 | | 110 | 11 | 6 | 6 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction | | | | 335 | 52 | 26 | 25 |
| | | Soluble Leachate Fraction | | | | 185 | 49 | 25 | 24 |

Table 34
Migration and Attenuation of Calcium in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/ Interfacing Soil | Sample Type | Sampling Date | | | | | | |
|---------------|---------------------------------------|---------------------------|---------------|--------|---------|---------|---------|---------|---------|
| | | | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction | | 34 | | 500 | 424 | 838 | 1,363 |
| | | Soluble Leachate Fraction | | 32 | | 205 | 420 | 717 | 1,272 |
| | | Interstitial Water | | | | 115 | 101 | | |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction | | 44 | | 475 | 555 | 1,340 | 1,650 |
| | | Soluble Leachate Fraction | | 26 | | 310 | 545 | 1,010 | 1,260 |
| | | Interstitial Water | | 204 | | 210 | 192 | 130 | 154 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction | | 780 | | 1,070 | 959 | 1,460 | 1,400 |
| | | Soluble Leachate Fraction | | 760 | | 970 | 788 | 1,270 | 1,120 |
| | | Interstitial Water | | 161 | | 180 | 172 | 65 | 60 |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction | | 36 | | 260 | 177 | 222 | 232 |
| | | Soluble Leachate Fraction | | 28 | | 130 | 141 | 120 | 177 |
| | | Interstitial Water | | 110 | | 125 | 138 | 18 | 128 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction | 30 | 44 | | 390 | 202 | 235 | 204 |
| | | Soluble Leachate Fraction | | 41 | | 170 | 172 | 134 | 160 |
| | | Interstitial Water | | 110 | | 165 | 116 | 50 | 120 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction | | 175 | | 195 | 485 | 656 | 934 |
| | | Soluble Leachate Fraction | | 153 | | 55 | 182 | 404 | 455 |
| | | Interstitial Water | | 211 | | 241 | 227 | 230 | 114 |
| 7 | --/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction | | | | 220 | 141 | 232 | 280 |
| | | Soluble Leachate Fraction | | | | 85 | 111 | 154 | 161 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction | | 202 | | 970 | 1,232 | 3,606 | 4,290 |
| | | Soluble Leachate Fraction | | 156 | | 805 | 1,192 | 2,560 | 2,270 |
| | | Interstitial Water | | 221 | | 260 | 303 | 226 | 222 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction | 205 | 196 | | 460 | 333 | 320 | 306 |
| | | Soluble Leachate Fraction | | 145 | | 320 | 76 | 103 | 123 |
| | | Interstitial Water | | 121 | | 110 | 172 | 48 | 94 |
| 10 | --/Perkins Loam (Soil Blank Column) | Total Leachate Fraction | | | | 335 | 303 | 360 | 366 |
| | | Soluble Leachate Fraction | | | | 185 | 145 | 280 | 300 |

Table 35
Solubility Products of Calcium Constituents
in the Final Dredged Material Leachate

| Column Number | Chemical Species | | Solubility Products | | |
|---------------|-----------------------|-----------------------|---------------------|--------------|--------------|
| | $[Ca^{2+}]$ (M) | $[CO_3^{2-}]$ (M) | K_1 | $(K_{sp})_1$ | $(K_{sp})_2$ |
| 2 | 3.85×10^{-3} | 4.44×10^{-4} | $10^{-5.8}$ | $10^{-6.5}$ | $10^{-6.9}$ |
| 3 | 1.5×10^{-3} | 1.83×10^{-4} | $10^{-6.6}$ | $10^{-7.3}$ | $10^{-7.7}$ |
| 4 | 3.2×10^{-3} | 3.48×10^{-5} | $10^{-7.0}$ | $10^{-7.7}$ | $10^{-8.1}$ |
| 5 | 3×10^{-3} | 2.5×10^{-5} | $10^{-7.1}$ | $10^{-7.9}$ | $10^{-8.2}$ |
| 6 | 2.85×10^{-3} | 2.3×10^{-4} | $10^{-6.2}$ | $10^{-6.9}$ | $10^{-7.3}$ |
| 8 | 5.5×10^{-3} | 1.43×10^{-4} | $10^{-6.1}$ | $10^{-6.8}$ | $10^{-7.2}$ |
| 9 | 2.35×10^{-3} | 5.6×10^{-5} | $10^{-6.9}$ | $10^{-7.6}$ | $10^{-8.0}$ |

where $K_1 = [Ca^{2+}][CO_3^{2-}]$
 $(K_{sp})_1 = \gamma Ca^{2+} \cdot \gamma CO_3^{2-} [Ca^{2+}][CO_3^{2-}]$
 $= 0.9 \times 0.2 K_1$
 $(K_{sp})_2 = 0.9 \times 0.09 K_1$

Table 36
Migration and Attenuation of Magnesium in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
|---------------|--------------------------------------|--|--------|-------------------|---------|-------------------|-------------------|-------------------|-------------------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 10 7 | | 61 42 278 | 105 86 303 | 126 114 | 160 160 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 9 6 400 | | 91 62 640 | 126 90 444 | 142 142 448 | 171 160 416 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 252 258 365 | | 360 260 560 | 525 191 379 | 490 479 501 | 484 436 383 |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 11 8 64 | | 31 17 39 | 33 14 45 | 3.5 3.3 7.3 | 3.3 2.9 5.3 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 7 | 12 9 62 | | 42 23 46 | 37 21 51 | 3.6 3.0 3.3 | 3.4 3.0 5.2 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 248 200 445 | | 226 168 614 | 219 200 465 | 351 327 393 | 382 373 444 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | | 12.7 14.7 | 22 20 | 3.3 3.2 | 3.6 3.3 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 236 200 600 | | 526 430 840 | 460 328 728 | 743 225 776 | 775 739 776 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 187 | 252 215 62 | | 217 148 35 | 153 89 57 | 138 108 4.2 | 151 145 3.4 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | | 140 139 | 143 141 | 164 163 | 171 163 |

Table 37
Solubilization Calculations of Magnesium Solids

Brucite ($\text{Mg}(\text{OH})_2$):

$$[\text{Mg}^{2+}] = \frac{10^{-11.6}}{[\text{OH}^-]^2} = 2.5 \text{ M} = 60,000 \text{ ppm} \quad (30)$$

Nesquehonite (MgCO_3):

$$[\text{Mg}^{2+}] = \frac{10^{-5.4}}{[\text{CO}_3^{2-}]} \quad (31)$$

| Column Number | Chemical Species | | | Analyzed Value (ppm) |
|------------------|----------------------------------|--------------------------------|--------------------------------|-------------------------|
| | $[\text{CO}_3^{2-}] \text{ (M)}$ | $[\text{Mg}^{2+}] \text{ (M)}$ | $\text{Mg}^{2+} \text{ (ppm)}$ | |
| 2 | 4.44×10^{-4} | 8.97×10^{-3} | 215 | 416 |
| 3 | 1.83×10^{-4} | 2.18×10^{-2} | 522 | 501 |
| 4 | 3.48×10^{-5} | 1.14×10^{-1} | 2,753 | 5.3 |
| 5 | 2.5×10^{-5} | 1.59×10^{-2} | 3,820 | 5.2 |
| 6 | 2.3×10^{-4} | 1.73×10^{-2} | 415 | 444 |
| 8 | 1.43×10^{-4} | 2.78×10^{-2} | 668 | 776 |
| 9 | 5.6×10^{-5} | 7.11×10^{-2} | 1,710 | 3.4 |

Dolomite ($\text{CaMg}(\text{CO}_3)_2$):

$$[\text{Mg}^{2+}] = \frac{10^{-16.7}}{[\text{Ca}^{2+}][\text{CO}_3^{2-}]} \quad (32)$$

(Continued)

Table 37

(Concluded)

| Column Number | Chemical Species | | | |
|---------------|--------------------------|------------------------|------------------------|--------------------------|
| | $[\text{CO}_3^{2-}]$ (M) | $[\text{Ca}^{2+}]$ (M) | $[\text{Mg}^{2+}]$ (M) | $[\text{Mg}^{2+}]$ (ppm) |
| 2 | 4.44×10^{-4} | 3.85×10^{-3} | 1.17×10^{-11} | 2.8×10^{-7} |
| 3 | 1.83×10^{-4} | 1.5×10^{-3} | 7.27×10^{-11} | 1.8×10^{-6} |
| 4 | 3.48×10^{-5} | 3.2×10^{-3} | 1.79×10^{-10} | 4.35×10^{-6} |
| 5 | 2.5×10^{-5} | 3×10^{-3} | 2.7×10^{-10} | 6.46×10^{-6} |
| 6 | 2.3×10^{-4} | 2.85×10^{-3} | 3.04×10^{-11} | 7.4×10^{-7} |
| 8 | 1.43×10^{-4} | 5.5×10^{-3} | 2.54×10^{-11} | 6.16×10^{-7} |
| 9 | 5.6×10^{-5} | 2.35×10^{-3} | 1.52×10^{-10} | 3.68×10^{-6} |

Hydromagnesite $(\text{Mg}_4(\text{CO}_3)_2(\text{OH})_2 \cdot 3\text{H}_2\text{O})$:

$$[\text{Mg}^{2+}] = \left(\frac{10^{-29.5}}{[\text{OH}^-]^2 [\text{CO}_3^{2-}]^3} \right)^{1/4} \quad (33)$$

$$= \frac{4.22 \times 10^{-5}}{[\text{CO}_3^{2-}]^{3/4}}$$

| Column Number | Chemical Species | | | Analyzed Value (ppm) |
|---------------|--------------------------|------------------------|--------------------------|----------------------|
| | $[\text{CO}_3^{2-}]$ (M) | $[\text{Mg}^{2+}]$ (M) | $[\text{Mg}^{2+}]$ (ppm) | |
| 2 | 4.44×10^{-4} | 1.38×10^{-2} | 331 | 416 |
| 3 | 1.83×10^{-4} | 2.68×10^{-2} | 643 | 501 |
| 4 | 3.48×10^{-5} | 9.31×10^{-2} | 2,230 | 5.3 |
| 5 | 2.5×10^{-5} | 1.19×10^{-1} | 2,860 | 5.2 |
| 6 | 2.3×10^{-4} | 2.26×10^{-2} | 542 | 444 |
| 8 | 1.43×10^{-4} | 3.22×10^{-2} | 774 | 776 |
| 9 | 5.6×10^{-5} | 6.51×10^{-2} | 1,560 | 3.4 |

Table 38
Migration and Attenuation of Chloride in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/ Interfacial Soil | Sample Type | Sampling Date | | | | | | |
|---------------|---|--|---------------|----------------------------|---------------------------|----------------------------|------------------|-----------------|-----------|
| | | | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 44 6,800 | | | 2,000 1,700 | 2,500 | 4,400 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 44 10,000 | 410 9,000 | 10,000 | 2,700 2,700 | 3,700 8,200 | 4,800 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 10,000 10,000 10,000 | 10,000 10,000 8,400 | 10,300 10,300 10,300 | 10,500 10,500 | 15,000 9,700 | |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 45 | 43 130 | 120 105 | 140 160 58 | 260 | 190 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 30 | 24 84 | 12 100 | 160 110 | 175 110 68 | 260 46 | 185 45 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 1,000 10,000 | 1,025 1,500 10,000 | 1,220 10,300 | 1,350 | 3,500 9,600 | 3,400 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 43 29 | 130 | 45 | 74 | 45 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 840 10,000 | 840 1,100 10,100 | 5,000 5,000 10,500 | 7,000 7,600 | 9,600 13,000 | |
| 9 | Grand Haven/Perk Ins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 560 | 780 660 140 | | 450 140 | 350 300 45 | 260 47 | 260 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 600 660 | 720 | 380 520 | 560 | 560 |

Table 39
Migration and Attenuation of Iron in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/ Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
|---------------|--|--|--------|---------------------|-----------------------|---------------------|-------------------|-------------------|-------------------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 5.5 5.3 | 3.9 | 2.4 1.8 0.2 | 5.2 1.6 0.8 | 113 17 | 115 18 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 3.5 2.7 1.3 | 30.0 5.9 0.5 | 56.0 1.0 0.4 | 106 3.1 0.8 | 130 0.8 0.5 | 135 35 0.5 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 77.2 74.0 1.1 | 166.8 144.4 0.2 | 65.0 1.1 0.5 | 1.5 1.4 0.8 | 108 40 0.3 | 48 0.6 0.7 |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 6.4 6.1 0.4 | 20.2 4.6 0.1 | 49.0 16.7 0.2 | 54 7.6 0.6 | 48 3.5 Nil | 55 4.5 Nil |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 1.2 | 2.3 1.8 0.4 | 1.4 0.2 0.1 | 57.5 13.0 0.3 | 66 11 0.4 | 55 11 0.2 | 61 23 Nil |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 4.6 0.8 1.0 | 3.6 0.8 0.5 | 4.9 0.8 0.4 | 41 0.4 1.1 | 40 0.5 0.5 | 30 0.5 0.5 |
| 7 | --/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 5.1 4.0 | 19.7 9.7 | 22 6 | 60 12 | 70 12 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 8.5 1.3 1.1 | 4.6 0.6 0.5 | 68.5 0.5 0.4 | 25 0.7 1.3 | 31 0.6 0.5 | 115 0.6 0.8 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 3.1 | 7.0 0.6 0.2 | 0.5 0.2 0.1 | 53.0 0.4 0.6 | 19 0.3 0.3 | 59 0.2 Nil | 63 0.2 Nil |
| 10 | --/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 7.8 1.6 | 16.2 0.2 | 23 0.3 | 41 0.5 | 46 0.2 |

Table 40
Migration and Attenuation of Manganese in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | Sampling Date | | | 1/28/77 |
|---------------|--------------------------------------|--|--------|-----------------------|-----------------------|-----------------------|---------------------|---------------------|----------------------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 7.2 8.2 | 22.8 | 43.5 43.0 2.2 | 73.5 68.3 0.3 | 95 66 | 127 120 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 6.6 6.2 1.1 | 26.2 28.4 1.2 | 53.0 35.0 1.4 | 92.4 89.3 0.7 | 113 105 0.25 | 136 121 0.26 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 127.0 125.0 0.7 | 104.6 105.6 0.7 | 128.0 122.0 1.8 | 110 108 0.8 | 115 97 0.55 | 96 83 0.5 |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 7.2 8.1 1.1 | 17.3 17.4 3.0 | 28.0 25.0 1.40 | 25.8 25 1.2 | 23 16.6 0.2 | 22.6 20.0 0.20 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 4.7 | 8.4 9.0 1.5 | 0.5 0.1 4.6 | 31.0 30.0 2.2 | 29.5 29.5 0.3 | 24 20 0.2 | 22.6 21.6 1.25 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 1.2 0.7 2.9 | 0.8 0.7 2.5 | 0.1 0.1 1.8 | 16 0.3 1.5 | 1.8 0.25 0.20 | 5.5 1.3 0.25 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 8.1 7.6 | 12.7 14.7 | 17.2 16.7 | 24.6 24 | 19.5 18 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 4.3 1.2 11.8 | 0.5 0.4 16.0 | 15.0 14.6 6.1 | 12.5 10.5 6 | 16.7 16.3 2.4 | 26.4 18.5 3.1 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 12.8 | 2.6 1.8 0.5 | 0.2 0.1 1.9 | 13.0 12.6 0.9 | 12 0.4 2.2 | 9.8 0.2 0.2 | 11.5 1.6 0.60 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 26.4 15.8 | 12.6 3.9 | 15 0.2 | 12.7 0.6 | 23.5 2.2 |

Table 41
Manganese Ligand Complexation Calculations

$$\begin{aligned}
 [\text{Mn}_T] &\approx [\text{Mn}^{2+}_f] + [\text{MnCl}^+_1] + [\text{MnCl}^0_2] + [\text{MnCl}^-_3] \quad (34) \\
 &\quad + [\text{MnHCO}^+_3] \\
 &\approx [\text{Mn}^{2+}_f] \left\{ 1 + 10^{1.08}[\text{Cl}^-] + 10^{1.52}[\text{Cl}^-]^2 + \right. \\
 &\quad \left. 10^{1.11}[\text{Cl}^-]^3 + 10^{1.8}[\text{HCO}_3] \right\}
 \end{aligned}$$

For saline dredged material, the relative importance among these soluble species is as follows:

$$\frac{[\text{Mn-Cl complexes}]}{[\text{Mn}_T]} \approx 74\%$$

$$\frac{[\text{MnHCO}^+_3]}{[\text{Mn}_T]} \approx 14\%$$

$$\frac{[\text{Mn}^{2+}_f]}{[\text{Mn}_T]} \approx 12\%$$

For fresh water dredged material, the following order can be calculated:

$$\frac{[\text{MnHCO}^+_3]}{[\text{Mn}_T]} \approx 54\%$$

$$\frac{[\text{Mn}^{2+}_f]}{[\text{Mn}_T]} \approx 45\%$$

$$\frac{[\text{Mn-Cl complexes}]}{[\text{Mn}_T]} \approx 1\%$$

Table 42
Migration and Attenuation of Cadmium in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
|---------------|--------------------------------------|--|--------|----------------------------|--------------------------|-------------------------|----------------------------|--------------------------|--------------------------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.0018 0.0013 | 0.006 | 0.024 0.008 0.006 | 0.0015 0.0012 0.0600 | 0.003 0.003 | 0.008 0.006 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.0011 0.006 0.146 | 0.004 0.003 0.160 | 0.036 0.002 0.002 | 0.0030 0.0030 0.0045 | 0.006 0.005 0.420 | 0.013 0.012 0.053 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.0152 0.0009 0.165 | 0.120 0.086 0.064 | 0.006 0.002 0.004 | 0.0011 0.0010 0.0010 | 0.062 0.051 0.058 | 0.023 0.021 0.067 |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.0021 0.0006 0.0006 | 0.005 0.001 0.003 | 0.015 0.002 0.003 | 0.0005 0.0002 0.0002 | 0.001 Nil Nil | 0.001 Nil Nil |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0017 | 0.0020 0.0004 0.0006 | 0.001 0.0004 0.003 | 0.028 0.002 0.002 | 0.005 Nil 0.0004 | 0.002 Nil Nil | 0.001 Nil Nil |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.0020 0.0019 0.123 | 0.006 0.006 0.200 | 0.049 0.004 0.002 | 0.0035 0.0030 0.0191 | 0.006 0.006 0.063 | 0.007 0.0065 0.060 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 0.0009 0.0004 | 0.0004 Nil | 0.0010 0.0002 | 0.002 Nil | 0.001 Nil |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.0026 0.0020 0.106 | 0.008 0.006 0.640 | 0.029 0.002 0.002 | 0.0115 0.0100 0.0190 | 0.0275 0.021 0.097 | 0.029 0.023 0.016 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0034 | 0.0034 0.0021 0.0009 | 0.026 0.004 0.002 | 0.050 0.001 0.003 | 0.0032 0.0012 0.0025 | 0.003 0.001 Nil | 0.003 Nil Nil |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 0.002 0.002 | 0.0012 0.0004 | 0.0032 0.0024 | 0.0045 0.0025 | 0.0045 0.0015 |

Table 43

Migration and Attenuation of Copper in Simulating Dredged Material

Disposal to Upland Areas - Phase I

(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
|---------------|---------------------------------------|--|--------|-------------------------|----------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.017 0.007 | 0.34 | 0.024 0.008 0.006 | 0.010 0.001 0.003 | 0.014 0.012 | 0.013 0.002 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.010 0.015 0.030 | 0.23 0.01 0.06 | 0.036 0.002 0.002 | 0.220 0.002 0.001 | 0.009 0.002 0.002 | 0.011 0.002 0.002 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.019 0.004 0.046 | 0.14 0.07 0.06 | 0.006 0.002 0.004 | 0.006 0.001 0.001 | 0.008 0.003 0.001 | 0.029 0.027 0.001 |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.024 0.008 0.009 | 0.14 0.01 0.01 | 0.015 0.003 0.003 | 0.018 0.001 0.010 | 0.010 0.003 0.002 | 0.014 0.003 0.002 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.015 | 0.016 0.010 0.018 | 0.19 0.01 0.02 | 0.028 0.002 0.002 | 0.012 0.002 0.001 | 0.013 0.002 0.002 | 0.022 0.003 0.001 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.042 0.010 0.038 | 0.12 0.14 0.06 | 0.049 0.004 0.002 | 0.010 0.002 0.004 | 0.012 0.001 0.001 | 0.008 0.001 0.001 |
| 7 | --/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 0.02 0.01 | 0.058 0.003 | 0.013 0.003 | 0.021 0.005 | 0.012 0.005 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.034 0.004 0.065 | 0.28 0.02 0.08 | 0.029 0.002 0.002 | 0.022 0.003 0.001 | 0.008 0.003 0.007 | 0.009 0.004 0.001 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.092 | 0.021 0.004 0.012 | 0.36 0.01 0.01 | 0.050 0.001 0.003 | 0.008 0.001 0.001 | 0.008 0.001 0.001 | 0.007 0.001 0.001 |
| 10 | --/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 0.03 0.02 | 0.032 0.002 | 0.006 0.001 | 0.010 0.003 | 0.012 0.001 |

Table 44
Migration and Attenuation of Mercury in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppb)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | Sampling Date | | | | | | |
|---------------|---|--|---------------|-------------------|--------------------|-----------------|--------------------|--------------------|--------------------|
| | | | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 3.2 0.3 | 8.7 | 1 Nil | 1.3 0.2 | 8.4 0.5 | 23.7 0.4 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 1.2 0.3 0.3 | 4.7 0.8 Nil | 11 1 Nil | 24 Nil Nil | 12.7 1.0 Nil | 24.4 1.2 0.5 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.7 0.3 4.5 | 4.3 0.2 Nil | 2 1 1 | 18 Nil Nil | 18.4 0.2 1.1 | 5.3 0.8 Nil |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.9 0.4 0.2 | 5.5 1.2 0.2 | 5 Nil 4 | 4 Nil 1.2 | 6.3 1.8 1.0 | 4.5 1.7 Nil |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 1.1 | 0.4 Nil 1.1 | 7.7 1.2 0.2 | 3 1 Nil | 2.7 0.8 Nil | 4.4 0.5 0.1 | 12.0 0.3 0.3 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.8 0.5 2.5 | 16.7 0.4 0.2 | 9 3 2 | 16.7 0.7 0.8 | 6.5 1.4 0.8 | 7.2 1.5 1.0 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 3.3 0.6 | 2 Nil | 6.2 0.7 | 19.3 2.4 | 3.5 0.5 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.4 0.3 2.3 | 5.0 2.3 0.3 | 3 Nil 1 | 3.7 0.4 0.4 | 16.2 0.9 0.8 | 7.5 2.5 0.5 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.5 | 0.8 0.4 3.1 | 33 2.5 0.2 | 5 Nil Nil | 0.7 Nil Nil | 10.9 0.2 0.5 | 4.9 0.4 0.2 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 6.0 0.4 | 1 1 | 0.3 0.1 | 13.2 .4 | 4.5 0.7 |

Table 45
Migration and Attenuation of Lead in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
|---------------|--------------------------------------|--|--------|-------------------------|----------------------|-------------------------|-------------------------|------------------------|-------------------------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.008 0.004 | 0.06 | 0.002 0.002 0.275 | 0.009 0.008 0.220 | 0.02 0.02 | 0.044 0.044 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.008 0.003 0.190 | 0.06 0.02 0.18 | 0.007 0.005 0.255 | 0.028 0.019 0.270 | 0.04 0.036 0.27 | 0.062 0.058 0.248 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.078 0.038 0.030 | 0.38 0.34 0.12 | 0.502 0.485 | 0.360 0.300 0.360 | 0.35 0.33 0.36 | 0.43 0.45 0.30 |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.052 0.004 0.025 | 0.03 0.02 0.02 | 0.003 0.001 0.002 | 0.009 0.003 0.001 | 0.006 M11 M11 | 0.014 0.004 M11 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.013 | 0.016 0.003 0.034 | 0.06 0.01 0.03 | 0.003 0.002 0.003 | 0.003 0.001 0.003 | 0.006 M11 M11 | 0.018 M11 M11 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.023 0.010 0.120 | 0.11 0.03 0.21 | 0.004 0.003 | 0.016 0.010 0.285 | 0.03 0.332 | 0.036 0.036 0.27 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 0.04 0.01 | 0.009 0.002 | 0.009 0.003 | 0.017 M11 | 0.011 M11 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.015 0.008 0.160 | 0.08 0.06 0.16 | 0.060 0.045 | 0.088 0.055 0.435 | 0.094 0.094 0.46 | 0.14 0.14 0.53 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.020 | 0.020 0.011 0.025 | 0.09 0.03 0.03 | 0.013 0.003 0.002 | 0.008 0.003 0.003 | 0.01 0.005 M11 | 0.034 0.003 0.003 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 0.01 0.01 | 0.008 0.007 | 0.009 0.008 | 0.015 0.01 | 0.016 0.007 |

Table 46
Migration and Attenuation of Zinc in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
|---------------|--------------------------------------|--|--------|----------------------|----------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.20 0.08 | 2.24 | 0.435 0.250 0.125 | 0.165 0.150 0.030 | 0.210 0.175 | 0.240 0.240 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.26 0.21 0.04 | 0.43 0.12 0.04 | 0.240 0.040 0.070 | 0.300 0.265 0.800 | 0.350 0.340 0.075 | 0.400 0.270 0.060 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.31 0.16 0.08 | 0.19 0.06 0.13 | 0.165 0.110 0.070 | 0.364 0.140 0.075 | 0.135 0.110 0.090 | 0.210 0.115 0.025 |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.20 0.12 0.04 | 0.27 0.06 0.02 | 0.210 0.085 0.020 | 0.165 0.060 0.020 | 0.100 0.025 0.010 | 0.125 0.060 0.020 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.08 | 0.24 0.18 0.05 | 0.24 0.11 0.03 | 0.215 0.125 0.060 | 0.185 0.135 0.030 | 0.120 0.075 0.010 | 0.150 0.080 0.020 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.09 0.04 0.05 | 0.14 0.07 0.06 | 0.135 0.060 0.110 | 0.180 0.040 0.505 | 0.160 0.130 0.060 | 0.175 0.070 0.075 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 0.18 0.11 | 0.185 0.110 | 0.560 0.508 | 0.245 0.160 | 0.210 0.115 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.14 0.03 0.06 | 0.12 0.06 0.06 | 0.100 0.085 0.085 | 0.175 0.095 0.080 | 0.080 0.080 0.100 | 0.160 0.130 0.120 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.20 | 0.21 0.02 0.02 | 0.28 0.03 0.04 | 0.120 0.035 0.130 | 0.075 0.035 0.425 | 0.070 0.010 0.025 | 0.090 0.025 0.020 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | | 0.10 0.04 | 0.110 0.020 | 0.075 0.040 | 0.068 0.010 | 0.075 0.025 |

Table 47
Migration and Attenuation of Chlorinated Pesticides
In Simulating Dredged Material Disposal to Upland Areas - Phase I
(all values in ppb)

| Column Number | Dredged /Interfacing Material/ Soil | Sample Type | Sampling Date | | | | | | |
|---------------|--------------------------------------|--|---------------|----------------|------------------|---------|---------|------------|---------|
| | | | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 1 2.2 10 | <2.2 3 2.2 | | | <1.0 25 | <8 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | | 3 | | | <8 | 20 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 1 | 1 | <1.0 | | <8 | |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 12 | <2.2 | | | <8 | <8 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 2 | 3 2.2 3 | <2.2 | | | <8 | <8 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | | <1 | <1.0 | | <8 | <8 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | | 6 | 15 | | <8 | 20 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 2.5 2.2 | 2 | <1.0 | | <8 | |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 2 | 12 2.2 | 2.2 | | | <8 | <8 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | <2.2 | 1 | 8 | | <8 | <8 |

Table 48
Migration and Attenuation of Polychlorinated Biphenyls (as Aroclor 1254)
in Simulating Dredged Material Disposal to Upland Areas - Phase I
(all values in ppb)

| Column Number | Dredged Material/ Soil | Sample Type | Sampling Date | | | | | | |
|---------------|---|--|---------------|--------|---------|---------|---------|------------------|---------|
| | | | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 |
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | <0.02 | <1 | <0.02 | <0.5 | <0.09 | <0.09 |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | <0.02 | <0.02 | <0.02 | <0.5 | <0.09 | <0.09 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | <0.02 | <0.02 | <0.02 | <0.5 | <0.025 <0.025 | <0.09 |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 1.9 | <1 | | <0.5 | <0.09 | <0.09 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 1.77 | <0.02 | <1 | <0.02 | <0.5 | <0.09 | <0.09 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | <1 | <1 | | <0.5 | <0.09 | <0.09 |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | 2.6 | 2.45 | <0.02 | <0.02 | <0.09 | <0.09 |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | <0.02 | <0.02 | | <0.5 | <0.025 <0.025 | <0.09 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | <0.02 | <1 | | <0.02 | <0.5 | <0.09 | <0.09 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction Soluble Leachate Fraction | | <0.02 | | | <0.5 | <0.09 | <0.09 |

Table 49
Detection Limits of Chlorinated Hydrocarbons

| <u>Constituents</u> | <u>Detection Limit (ppb)*</u> |
|---------------------|-------------------------------|
| p,p'DDE | 8 |
| o,p'DDE | 11 |
| p,p'DDD | 15 |
| p,p'DDT | 26 |
| o,p'DDT | 16 |
| Aldrin | 6 |
| Heptachlor | 8 |
| Heptachlor Epoxide | 6 |
| Endrin | 90 |
| Dieldrin | 6 |
| Chlordane | 20 |
| PCB 1242 | 80 |
| PCB 1252 | 130 |
| PCB 1260 | 13 |

* Injection volume = 0.3 μ l.

Table 50
Ion Products of pH Controlling Constituents

| Column Number | Ion Products | | | | | |
|---------------|-----------------------|-----------------------|--------------|-----------------------|-----------------------|--------------|
| | $[Ca^{2+}]_{in}(M)$ | $[HCO_3^-]_{in}(M)$ | K_{in} | $[Ca^{2+}]_{out}(M)$ | $[HCO_3^-]_{out}(M)$ | K_{out} |
| 2 | 3.85×10^{-3} | 2.8×10^{-2} | $10^{-3.97}$ | 3.15×10^{-2} | 7.38×10^{-3} | $10^{-3.63}$ |
| 3 | 1.5×10^{-3} | 2.3×10^{-2} | $10^{-4.46}$ | 2.8×10^{-2} | 5.6×10^{-3} | $10^{-3.80}$ |
| 4 | 3.2×10^{-3} | 1.1×10^{-2} | $10^{-4.45}$ | 4.43×10^{-3} | 8.24×10^{-3} | $10^{-4.44}$ |
| 5 | 3×10^{-3} | 1×10^{-2} | $10^{-4.52}$ | 4×10^{-3} | 6.78×10^{-3} | $10^{-4.57}$ |
| 6 | 2.85×10^{-3} | 2.9×10^{-2} | $10^{-4.08}$ | 1.14×10^{-2} | 2.39×10^{-2} | $10^{-3.56}$ |
| 8 | 5.5×10^{-3} | 2.27×10^{-2} | $10^{-3.9}$ | 5.68×10^{-2} | 1.77×10^{-2} | $10^{-3.0}$ |
| 9 | 2.35×10^{-3} | 8.89×10^{-3} | $10^{-4.68}$ | 3.08×10^{-3} | 2.62×10^{-2} | $10^{-4.09}$ |
| | | | | | | $10^{-2.6}$ |
| | | | | | | $10^{-2.5}$ |
| | | | | | | $10^{-2.19}$ |
| | | | | | | $10^{-1.7}$ |
| | | | | | | $10^{-3.5}$ |
| | | | | | | $10^{-4.1}$ |
| | | | | | | $10^{-3.1}$ |

where $[]_{in}$ = Concentration of constituent in the interstitial water (influent of the interfacing soil system)

$[]_{out}$ = Concentration of constituents in the leachates (in effluent of the interfacing soil system)

$$K_x = \frac{[Ca^{2+}]_x [HCO_3^-]_x}{[H^+]}$$

Table 51
Solubility Products of Carbonate Species

| Column Number | Alk (meq/l) | pH | Chemical Species | | | | | |
|---------------|-------------|------|-----------------------------------|----------------------------------|-------------------------|-------------------------|-------------------------|--------------------------|
| | | | HCO ₃ ⁻ (M) | CO ₃ ⁼ (M) | Ca ²⁺ (M) | Mg ²⁺ (M) | K ₁ | K ₂ |
| 1 | 5.6 | 6.97 | 5.59 x 10 ⁻³ | 5.23 x 10 ⁻⁶ | 3.18 x 10 ⁻² | 6.58 x 10 ⁻³ | 4.49 x 10 ⁻⁸ | 4.62 x 10 ⁻¹⁶ |
| 2 | 7.4 | 6.83 | 7.38 x 10 ⁻³ | 5 x 10 ⁻⁶ | 3.15 x 10 ⁻² | 6.58 x 10 ⁻³ | 4.25 x 10 ⁻⁸ | 4.2 x 10 ⁻¹⁶ |
| 3 | 5.6 | 6.87 | 5.6 x 10 ⁻³ | 4.16 x 10 ⁻⁶ | 2.8 x 10 ⁻² | 1.79 x 10 ⁻² | 3.14 x 10 ⁻⁸ | 7.02 x 10 ⁻¹⁶ |
| 4 | 8.24 | 7.20 | 8.34 x 10 ⁻³ | 1.36 x 10 ⁻⁵ | 4.43 x 10 ⁻³ | 1.19 x 10 ⁻⁴ | 1.57 x 10 ⁻⁸ | 7.35 x 10 ⁻¹⁸ |
| 5 | 6.78 | 6.83 | 6.78 x 10 ⁻³ | 4.59 x 10 ⁻⁶ | 4 x 10 ⁻³ | 1.23 x 10 ⁻⁴ | 4.96 x 10 ⁻⁹ | 8.37 x 10 ⁻¹⁹ |
| 6 | 24 | 7.63 | 2.39 x 10 ⁻² | 1.02 x 10 ⁻⁴ | 1.14 x 10 ⁻² | 1.53 x 10 ⁻² | 3.14 x 10 ⁻⁷ | 1.47 x 10 ⁻¹³ |
| 7 | 10.2 | 6.36 | 1.02 x 10 ⁻² | 2.34 x 10 ⁻⁶ | 4.03 x 10 ⁻³ | 1.36 x 10 ⁻⁴ | 2.55 x 10 ⁻⁹ | 2.43 x 10 ⁻¹⁹ |
| 8 | 17.8 | 7.70 | 1.77 x 10 ⁻² | 8.89 x 10 ⁻⁵ | 5.68 x 10 ⁻² | 3.04 x 10 ⁻² | 1.36 x 10 ⁻⁶ | 1.10 x 10 ⁻¹² |
| 9 | 26.4 | 7.80 | 2.62 x 10 ⁻² | 1.66 x 10 ⁻⁴ | 3.08 x 10 ⁻³ | 5.97 x 10 ⁻³ | 1.38 x 10 ⁻⁷ | 4.12 x 10 ⁻¹⁴ |
| 10 | 25.8 | 7.55 | 2.57 x 10 ⁻² | 9.14 x 10 ⁻⁵ | 7.5 x 10 ⁻³ | 6.71 x 10 ⁻³ | 1.85 x 10 ⁻⁷ | 3.42 x 10 ⁻¹⁴ |

where $K_1 = \frac{[Ca^{2+}] \cdot [CO_3^{2-}]}{[Ca^{2+}] \cdot [CO_3^{2-}]}$

$K_2 = \frac{[Ca^{2+}] \cdot [Mg^{2+}] \cdot [CO_3^{2-}]}{[Ca^{2+}] \cdot [Mg^{2+}] \cdot [CO_3^{2-}]}$

(assuming $[Ca^{2+}]$ and $[Mg^{2+}]$ are 0.9 and $[CO_3^{2-}]$ is 0.3)

AD-A056 897

SCS ENGINEERS LONG BEACH CALIF

F/G 13/2

A STUDY OF LEACHATE FROM DREDGED MATERIAL IN UPLAND AREAS AND/O--ETC(U)

JUN 78 J L MANG, J C LU, R J LOFY

DACW39-76-C-0069

UNCLASSIFIED

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NL

4 OF 5

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Table 52

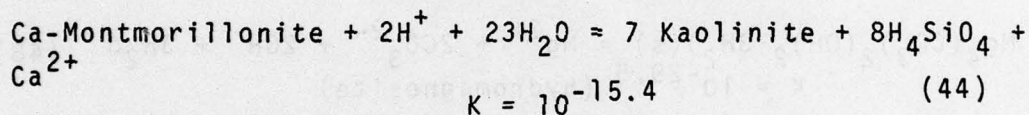
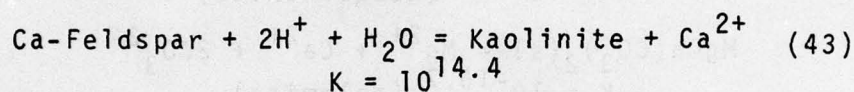
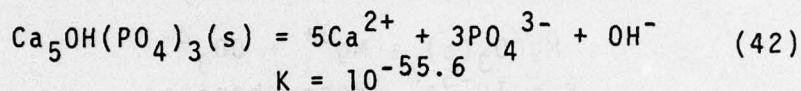
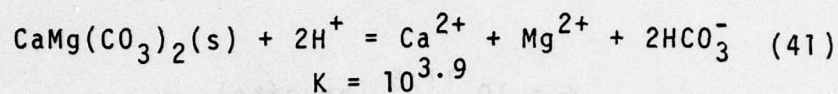
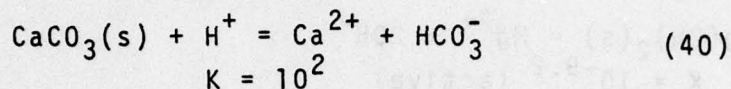
Calcium Solids and Related Thermodynamic Data

Table 53
Magnesium Solids and Related Solubility Products



$$K = 10^{-11.6} \text{ (brucite)}$$

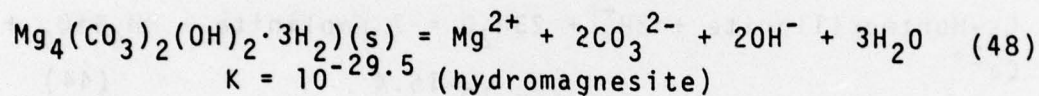
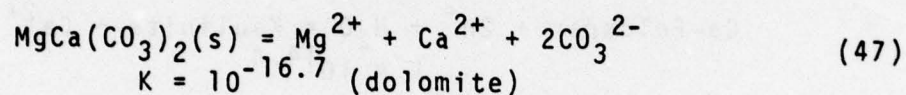
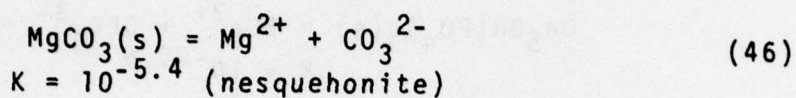


Table 54
Possible Soluble Magnesium Levels under Different
Controlling Solids

| Controlling Solid | Lake Arrowhead Soil | Perkins Soil |
|----------------------|---------------------|-------------------|
| active hydroxide | 3×10^{10} | 1.2×10^8 |
| brucite | 1×10^8 | 4.9×10^5 |
| nesquehonite | 41,300 | 1,060 |
| dolomite | 22 | 0.007 |
| hydromagnesite | 26.7 | 0.00007 |

Table 55
Manganese Solids Solubility Calculations

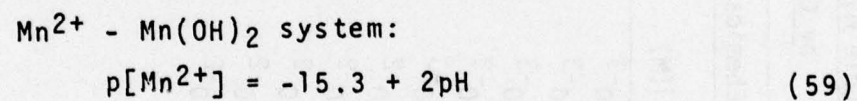
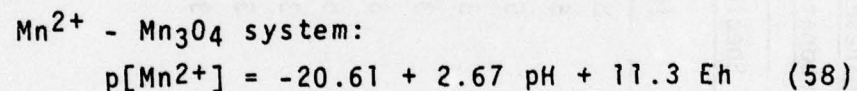
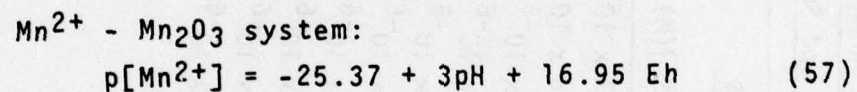
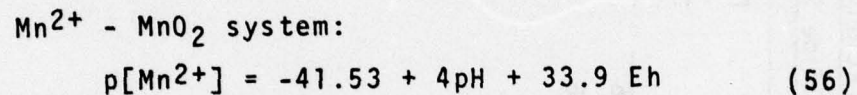
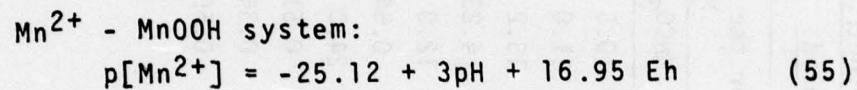
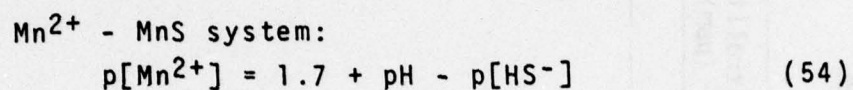
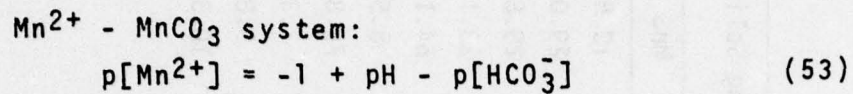


Table 56
Soluble Manganese Concentrations Controlled
by Carbonate and Sulfide Solids

| Column Number | Chemical Species | | | For the Controlling Solid | |
|------------------|------------------|------------------------------|---------------------------|---------------------------|--------------|
| | pH | $[\text{HCO}_3^-](\text{M})$ | $[\text{HS}^-](\text{M})$ | MnCO_3 | MnS |
| 1 | 6.97 | 5.6×10^{-3} | 8.7×10^{-6} | 10.5 | 13.5 |
| 2 | 6.83 | 7.4×10^{-3} | 5.6×10^{-6} | 11.0 | 29.0 |
| 3 | 6.87 | 5.6×10^{-3} | 5×10^{-6} | 13.2 | 29.6 |
| 4 | 7.20 | 8.2×10^{-3} | 3×10^{-6} | 4.23 | 23.1 |
| 5 | 6.83 | 6.8×10^{-3} | 3×10^{-6} | 12.0 | 54.1 |
| 6 | 7.63 | 2.4×10^{-2} | 3×10^{-6} | 0.54 | 8.58 |
| 7 | 6.36 | 1.0×10^{-2} | 6×10^{-6} | 24.0 | 79.8 |
| 8 | 7.70 | 1.8×10^{-2} | 3×10^{-6} | 0.61 | 7.3 |
| 9 | 7.80 | 2.6×10^{-2} | 3×10^{-6} | 0.34 | 5.8 |
| 10 | 7.55 | 2.6×10^{-2} | 3×10^{-6} | 0.60 | 10.3 |

Table 57
Free Cadmium Ion Concentrations under
Different Controlling Solids

| Column Number | $[\text{CO}_3^{=}]$ (M) | Chemical Species | | |
|------------------|-------------------------|-----------------------|------------------------|------------------------|
| | | $[\text{S}^{=}]$ (M) | Cd_{f1} (ppm) | Cd_{f2} (ppm) |
| 1 | 5.23×10^{-6} | 8.1×10^{-13} | 5.4×10^{-4} | 1.1×10^{-9} |
| 2 | 5×10^{-6} | 3.8×10^{-13} | 5.6×10^{-4} | 2.3×10^{-9} |
| 3 | 4.16×10^{-6} | 3.7×10^{-13} | 6.8×10^{-4} | 2.4×10^{-9} |
| 4 | 1.31×10^{-5} | 4.8×10^{-13} | 2.2×10^{-4} | 1.9×10^{-9} |
| 5 | 4.59×10^{-6} | 2×10^{-13} | 6.1×10^{-4} | 4.5×10^{-9} |
| 6 | 1.02×10^{-4} | 1.3×10^{-12} | 2.8×10^{-5} | 6.8×10^{-10} |
| 8 | 8.89×10^{-5} | 1.5×10^{-12} | 3.2×10^{-6} | 5.9×10^{-10} |
| 9 | 1.66×10^{-4} | 1.9×10^{-12} | 1.7×10^{-5} | 4.7×10^{-10} |

$$\text{where } [\text{Cd}_{f1}] = \frac{10^{-13.6}}{[\text{CO}_3^{=}]} \text{ (M)}$$

$$[\text{Cd}_{f2}] = \frac{10^{-26.1}}{[\text{S}^{=}]} \text{ (M)}$$

Table 58

Migration and Attenuation of Conductivity in Simulating Dredged Material

Disposal to Upland Areas - Phase I

(all values in $\mu\text{S}/\text{cm}$)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | Sampling Date | | | | |
|---------------|--------------------------------------|---------------------------|---------------------|---------------------|---------------------|---------------------|--------------------|
| | | | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 |
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction | | 0.013×10^4 | 0.115×10^4 | | 0.51×10^4 |
| | | Soluble Leachate Fraction | | 1.750×10^4 | | | |
| | | Interstitial Water | | | | | |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction | | 0.030×10^4 | 0.141×10^4 | | 0.73×10^4 |
| | | Soluble Leachate Fraction | | 1.280×10^4 | 0.135×10^4 | | 1.95×10^4 |
| | | Interstitial Water | | 2.710×10^4 | 2.450×10^4 | | 2.78×10^4 |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction | | 1.230×10^4 | 2.680×10^4 | | 2.06×10^4 |
| | | Soluble Leachate Fraction | | 3.400×10^4 | 2.610×10^4 | | 2.11×10^4 |
| | | Interstitial Water | | 0.040×10^4 | 1.902×10^4 | | 0.14×10^4 |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction | | 0.140×10^4 | 0.073×10^4 | | 0.10×10^4 |
| | | Soluble Leachate Fraction | | 0.030×10^4 | 0.066×10^4 | | 0.13×10^4 |
| | | Interstitial Water | | 0.040×10^4 | 0.160×10^4 | | 0.10×10^4 |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction | 0.040×10^4 | 0.130×10^4 | 0.070×10^3 | | 0.11×10^4 |
| | | Soluble Leachate Fraction | | 0.130×10^4 | 0.135×10^4 | | 0.12×10^4 |
| | | Interstitial Water | | 0.250×10^4 | 0.256×10^4 | | 0.77×10^4 |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction | | 2.600×10^4 | 0.250×10^4 | | 2.17×10^4 |
| | | Soluble Leachate Fraction | | | 2.620×10^4 | | 0.10×10^4 |
| | | Interstitial Water | | | 0.041×10^4 | 0.110×10^4 | |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction | | | 0.014×10^4 | | |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction | | 0.210×10^4 | 0.280×10^4 | | 1.75×10^4 |
| | | Soluble Leachate Fraction | | 0.260×10^4 | 0.310×10^4 | | 2.92×10^4 |
| | | Interstitial Water | | 3.720×10^4 | 3.800×10^4 | | 0.22×10^4 |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction | 0.249×10^4 | 0.220×10^4 | 0.220×10^4 | | 0.11×10^4 |
| | | Soluble Leachate Fraction | | 0.228×10^4 | 0.188×10^4 | | 0.13×10^4 |
| | | Interstitial Water | | 0.090×10^4 | 0.145×10^4 | | 0.29×10^4 |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction | | | 0.260×10^4 | 0.280×10^4 | |
| | | Soluble Leachate Fraction | | | 0.235×10^4 | | |

Table 59
Migration and Attenuation of Oil & Grease in Simulating Dredged Material
Disposal to Upland Areas - Phase I
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | Sampling Date | | | | | | | |
|---------------|--------------------------------------|---------------------------|---------------|--------|---------|---------|---------|---------|---------|------|
| | | | 8/3/76 | 9/1/76 | 9/30/76 | 11/4/76 | 12/3/76 | 1/14/77 | 1/28/77 | |
| 1 | Mobile/Lake Arrowhead | Total Leachate Fraction | | 16 | | | | 6.7 | | |
| | | Soluble Leachate Fraction | | | | | | | | |
| | | Interstitial Water | | | | | | | | |
| 2 | Sayerville/Lake Arrowhead | Total Leachate Fraction | | 12.6 | | | | 2.0 | | |
| | | Soluble Leachate Fraction | | | | | | | | |
| | | Interstitial Water | | | | | | | | |
| 3 | Seattle/Lake Arrowhead | Total Leachate Fraction | | 12.3 | 18 | 26.7 | | 8.9 | 36 | |
| | | Soluble Leachate Fraction | | | | | | | | |
| | | Interstitial Water | | | | | | | | |
| 4 | Grand Haven/Lake Arrowhead | Total Leachate Fraction | | 5.3 | | | | 3.0 | | |
| | | Soluble Leachate Fraction | | | | | | | | |
| | | Interstitial Water | | | | | | | | |
| 5 | Grand Haven/Lake Arrowhead | Total Leachate Fraction | 3.85 | 35 | | | | 23.3 | 25 | 5.7 |
| | | Soluble Leachate Fraction | | | | | | | | |
| | | Interstitial Water | | | | | | | | |
| 6 | Sayerville/Perkins Loam | Total Leachate Fraction | | 21.5 | 28.3 | 15.0 | | | | |
| | | Soluble Leachate Fraction | | | | | | | | |
| | | Interstitial Water | | | | | | | | |
| 7 | —/Lake Arrowhead (Soil Blank Column) | Total Leachate Fraction | | | 11.6 | | | | 31 | 37.1 |
| | | Soluble Leachate Fraction | | | | | | | | |
| 8 | Seattle/Perkins Loam | Total Leachate Fraction | | 12 | 18.6 | 1.3 | | | | |
| | | Soluble Leachate Fraction | | | | | | | | |
| | | Interstitial Water | | | | | | | | |
| 9 | Grand Haven/Perkins Loam | Total Leachate Fraction | 18.5 | 11.2 | | | | 3.3 | 4.3 | 22.8 |
| | | Soluble Leachate Fraction | | | | | | | | |
| | | Interstitial Water | | | | | | | | |
| 10 | —/Perkins Loam (Soil Blank Column) | Total Leachate Fraction | | | 12.8 | | | 5.9 | 37 | 10 |
| | | Soluble Leachate Fraction | | | | | | | | |

Table 60

Analytical Results of Pulse Flow Addition to Lysimeter
Columns 5 and 9 at the End of Nine Months of Experimentation
(all values in ppm unless otherwise noted)

| Constituents | Column 5 | | | Column 9 | | |
|--|---|---------------------------------|-----------------------|---|---------------------------------|-----------------------|
| | Dredged Material: Grand Haven Interfacing Soil: Lake Arrowhead Sandy Loam | | | Dredged Material: Grand Haven Soil: Perkins Loam | | |
| | Total Leachate Fraction | Soluble Leachate Fraction | Interstitial Water | Total Leachate Fraction | Soluble Leachate Fraction | Interstitial Water |
| Alkalinity | 160 | | 529 | 1190 | | 460 |
| pH | 6.54 | | 8.0 | 6.70 | | 7.80 |
| Conductivity ($\mu\Omega/\text{cm}$) | 0.06×10^4 | | 0.22×10^4 | 0.06×10^4 | | 0.21×10^4 |
| Oil and Grease | 29.5 | | | 31.7 | | |
| Total Organic Carbon (TOC) | 70 | | 500 | 620 | | 340 |
| Ammonia-Nitrogen ($\text{NH}_3\text{-N}$) | 0.89 | | 0.09 | 1.05 | | 3.98 |
| Nitrate Nitrogen ($\text{NO}_3\text{-N}$) | 0.12 | | 0.32 | 0.52 | | 0.58 |
| Organic Nitrogen | 55.4 | | 33.9 | 31.0 | | 32.6 |
| Total Kjeldahl Nitrogen | 56.3 | | 34.0 | 32.0 | | 36.6 |

(Continued)

(Concluded)

Table 60

| Constituents | Total Leachate Fraction | Soluble Leachate Fraction | Interstitial Water | Total Leachate Fraction | Soluble Leachate Fraction | Interstitial Water |
|---|-------------------------------|---------------------------------|-----------------------|-------------------------------|---------------------------------|-----------------------|
| Total Phosphorus | 0.11 | | 1.21 | 0.28 | | 6.33 |
| Orthophosphate (PO_4-P) | 0.06 | | 0.76 | 0.04 | | 0.61 |
| Chloride (Cl) | 100 | | 48 | 180 | | 29 |
| Calcium (Ca) | 91 | 55 | 565 | 91 | 58 | 436 |
| Magnesium (Mg) | 12 | 10 | 77 | 22 | 21 | 65 |
| Potassium (K) | 40 | 38 | 17 | 18 | 17 | 21 |
| Sodium (Na) | 45 | 43 | 82 | 28 | 27 | 88 |
| Cadmium (Cd) | 0.002 | 0.001 | 0.0002 | 0.0002 | N11 | 0.0002 |
| Copper (Cu) | 0.019 | 0.007 | 0.002 | 0.006 | 0.001 | 0.001 |
| Iron (Fe) | 5.3 | 4 | 0.08 | 3.2 | 0.07 | 0.04 |
| Lead (Pb) | 0.0014 | 0.001 | N11 | 0.0055 | N11 | N11 |
| Manganese (Mn) | 1.06 | 0.80 | 2.4 | 1.53 | 0.02 | 1.36 |
| Mercury (Hg) | 0.013 | 0.003 | 0.004 | 0.051 | 0.004 | 0.003 |
| Zinc (Zn) | 0.116 | 0.064 | 0.016 | 0.025 | 0.002 | 0.011 |
| Chlorinated Pesticides (PPB) | N.D.* | | | N.D.* | | |
| Polychlorinated Biphenyls (PPB as Arochlor 1254) | N.D.* | | | N.D.* | | |

*Not detectable.

Table 61
Chlorinated Pesticide Analytical Results of
Extracts from Polypropylene Beads
Removed from the Bottom of the Lysimeter Columns

| <u>Column</u> | <u>Bulk Extraction Results (mg/kg)</u> | <u>Theoretical Average Value in Total Leachate Fraction** (ppb)</u> |
|---------------|--|---|
| 1 | N.D.* | Trace |
| 2 | N.D.* | Trace |
| 3 | N.D.* | Trace |
| 4 | N.D.* | Trace |
| 5 | N.D.* | Trace |
| 6 | N.D.* | Trace |
| 7 | N.D.* | Trace |
| 8 | N.D.* | Trace |
| 9 | N.D.* | Trace |
| 10 | N.D.* | Trace |
| 11 | N.D.* | Trace |
| 12 | 7.0 | 0.001 |
| 13 | N.D.* | Trace |
| 14 | 3.0 | 0.005 |
| 15 | N.D.* | Trace |
| 16 | 7.5* | 0.023 |

*Not detectable.

**Bulk extraction concentration x average flow rate x
experimental duration.

Table 62
Polychlorinated Biphenyl Analytical Results
of Extracts from Polypropylene Beads Removed
from the Bottom of the Lysimeter Columns

| <u>Column</u> | <u>Bulk Extraction Results (mg/kg)</u> | <u>Theoretical Average Value in Total Leachate Fraction** (ppb)</u> |
|---------------|--|---|
| 1 | N.D.* | Trace |
| 2 | N.D.* | Trace |
| 3 | N.D.* | Trace |
| 4 | N.D.* | Trace |
| 5 | 85 | 1.06 |
| 6 | N.D.* | Trace |
| 7 | N.D.* | Trace |
| 8 | N.D.* | Trace |
| 9 | N.D.* | Trace |
| 10 | N.D.* | Trace |
| 11 | N.D.* | Trace |
| 12 | 170 | 0.66 |
| 13 | N.D.* | Trace |
| 14 | 60 | 0.09 |
| 15 | N.D.* | Trace |
| 16 | 90 | 0.15 |

*Not detectable.

**Bulk extraction concentration x average flow rate x experimental duration.

Table 63
Results of Analyses of Pure Waters of
Dredged Material and Interfacing Soils
(all values in ppm)

| Column Number | Cd | Cu | Fe | Hg | Mn | Pb | Zn | Na | K | Ca | Mg | 15" |
|---------------------------|--------|--------|------|--------|------|--------|--------|------|-----|------|-----|------|
| 1 Dredged Material | 0.0015 | 0.0015 | 17 | N11 | 1.5 | 0.180 | 0.003 | 3030 | 133 | 10 | 275 | 2.1 |
| 1 Interfacing Soil | 0.0013 | 0.0015 | 35 | N11 | 45 | 0.140 | 8.3 | 2530 | 100 | 1250 | 192 | 0.2 |
| 2 Dredged Material | 0.0013 | 0.0025 | 6 | N11 | 1.4 | 0.170 | 0.001 | 2530 | 41 | 141 | 384 | 2.2 |
| 2 Interfacing Soil | 0.0008 | 0.0025 | 110 | N11 | 46 | 0.150 | 3.2 | 2320 | 90 | 1490 | 242 | 0.18 |
| 3 Dredged Material | 0.0030 | 0.0020 | 1 | 0.0002 | 0.5 | 0.210 | 0.001 | 4550 | 165 | 35 | 445 | 3.5 |
| 3 Interfacing Soil | 0.0025 | 0.0040 | 20 | 0.0002 | 31 | 0.205 | 0.100 | 5660 | 150 | 902 | 442 | 0.16 |
| 4 Dredged Material | 0.0004 | 0.0024 | 0.5 | 0.0003 | 1.0 | 0.001 | 0.005 | 40 | 9 | 91 | 40 | 0.35 |
| 4 Interfacing Soil | 0.0012 | 0.0040 | 11 | N11 | 3.5 | 0.005 | 0.180 | 44 | 20 | 15 | 10 | 0.1 |
| 5 Dredged Material | 0.0004 | 0.0001 | 0.02 | N11 | 0.75 | 0.0002 | 0.0075 | 75 | 7.5 | 566 | 76 | 0.04 |
| 5 Interfacing Soil | N11 | 0.001 | 0.80 | N11 | 2.2 | 0.0015 | 0.0475 | 44 | 27 | 61 | 16 | 0.03 |
| 6 Top Dredged Material | 0.0012 | 0.0025 | 5 | N11 | 0.3 | 0.138 | 0.008 | 2320 | 100 | 20 | 237 | 0.1 |
| 6 Bottom Dredged Material | 0.0015 | 0.0021 | 8.5 | N11 | 0.8 | 0.186 | 0.60 | 4040 | 140 | 40 | 364 | 0.1 |
| 7 Top Interfacing Soil | 0.0017 | 0.0040 | 25 | N11 | 10.3 | 0.195 | 0.007 | 4340 | 122 | 707 | 495 | 0.1 |
| 7 Bottom Interfacing Soil | N11 | 0.0024 | 120 | N11 | 25 | 0.060 | 0.002 | 1410 | 50 | 2270 | 490 | 0.1 |
| 8 Interfacing Soil | 0.0004 | 0.0025 | 26 | N11 | 6.9 | 0.017 | 0.080 | 3 | 10 | 10 | 11 | 0.2 |
| 8 Dredged Material | 0.0023 | 0.0024 | 0.3 | N11 | 0.9 | 0.245 | -0.001 | 6060 | 24 | 38 | 478 | 0.1 |
| 9 Interfacing Soil | 0.0030 | 0.0020 | 114 | N11 | 33 | 0.295 | 0.005 | 5150 | 89 | 2470 | 473 | 0.1 |
| 9 Dredged Material | 0.0008 | 0.004 | N11 | N11 | 0.24 | 0.0027 | 0.155 | 80 | 6 | 856 | 89 | 0.08 |
| 10 Interfacing Soil | N11 | 0.001 | 0.91 | N11 | 0.41 | 0.0005 | 0.0015 | 63 | 43 | 76 | 71 | 0.02 |
| 10 Dredged Material | 0.0002 | 0.0024 | 0.6 | N11 | 15 | 0.005 | 0.001 | 80 | 14 | 151 | 111 | 0.1 |
| 11 Interfacing Soil | 0.0002 | 0.002 | 0.12 | N11 | 1.23 | 0.0032 | 0.0055 | 1220 | 82 | 232 | 200 | 0.1 |
| 11 Dredged Material | 0.0004 | 0.004 | 12.6 | N11 | 35 | 0.0027 | 0.0090 | 545 | 70 | 40 | 93 | 0.08 |
| 12 Dredged Material | 0.0005 | 0.001 | 0.09 | N11 | 0.13 | 0.0015 | 0.0550 | 1720 | 90 | 171 | 279 | 0.05 |
| 12 Interfacing Soil | 0.0002 | 0.001 | 0.10 | N11 | 0.05 | 0.0015 | 0.0050 | 227 | 50 | 126 | 238 | 0.05 |
| 13 Dredged Material | 0.0003 | 0.001 | 0.05 | N11 | 0.06 | 0.0021 | 0.0020 | 1725 | 91 | 126 | 287 | 0.06 |
| 13 Interfacing Soil | 0.0002 | 0.003 | 1.80 | N11 | 10.6 | 0.0015 | 0.0020 | 251 | 55 | 475 | 217 | 0.06 |
| 14 Dredged Material | 0.0002 | 0.003 | 0.75 | N11 | 0.37 | 0.0005 | 0.0030 | 1620 | 96 | 212 | 313 | 0.05 |
| 14 Interfacing Soil | 0.0006 | 0.005 | 0.18 | N11 | 5.5 | 0.0017 | 0.0020 | 253 | 26 | 384 | 200 | 0.04 |
| 15 Dredged Material | 0.003 | 0.002 | 1.4 | N11 | 1.7 | 0.0032 | 0.075 | 1700 | 96 | 414 | 242 | 0.08 |
| 15 Interfacing Soil | 0.0002 | 0.002 | 33 | N11 | 13 | 0.0015 | 0.003 | 232 | 58 | 485 | 208 | 0.05 |
| 16 Dredged Material | 0.0007 | 0.001 | 0.63 | N11 | 1.5 | 0.0027 | 0.0013 | 1720 | 87 | 343 | 258 | 0.11 |
| 16 Interfacing Soil | 0.0003 | 0.005 | 0.72 | N11 | 8 | 0.0026 | 0.0025 | 354 | 55 | 535 | 194 | 0.09 |

Table 64
Migration and Attenuation of pH in Simulating Dredged Material
Disposal to Upland Areas - Phase II

| Column Number | Dredged Material / Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|--|-------------------------|---------------|---------|--------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction | 7.65 | 7.24 | 7.53 |
| | | Interstitial Water | 8.55 | 7.78 | 7.84 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 7.78 | 7.54 | 7.48 |
| | | Interstitial Water | 7.01 | 7.03 | 7.64 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 7.17 | 7.60 | 7.29 |
| | | Interstitial Water | 7.25 | 7.45 | 7.22 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | 7.46 | 7.69 | 7.24 |
| | | Interstitial Water | 7.66 | 6.93 | 7.65 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | 6.97 | 7.51 | 8.02 |
| | | Interstitial Water | 7.30 | 7.59 | 7.43 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | 8.01 | 7.63 | 7.57 |
| | | Interstitial Water | 6.54 | 6.99 | 6.41 |

Table 65
Migration and Attenuation of Total Organic Carbon in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | 6/6/77 | 7/16/77 | 9/7/77 |
|---------------|--|-------------------------|--------|---------|--------|
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction | | 510 | 990 |
| | | Interstitial Water | 530 | 540 | 440 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 530 | 660 | 100 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 500 | 660 | 990 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | | | 680 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | | 300 | 800 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | | 730 | 120 |

Table 66

Migration and Attenuation of Alkalinity in Simulating Dredged Material

Disposal to Upland Areas - Phase II

(all values in ppm)

| Column Number | Dredged Material/ Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|---|---|---------------|-------------|-------------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Interstitial Water | 1220 | 258 1160 | 246 1090 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 290 | 330 | 260 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 140 | 210 | 300 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | | | 420 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | | 180 | 145 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | | 1258 | 1180 |

Table 67
Migration and Attenuation of Organic Nitrogen in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 6/6/77 | 7/16/77 | 9/7/77 |
|---------------|--|--|--------|-------------|--------------|
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 11.0 | 8.8 12.9 | 48.1 11.9 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 10.9 | 25.4 | 33.3 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 20.9 | 30.1 | 33.7 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | | | 4.5 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | | 22.9 | 4.5 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | | 27.3 | 21.2 |

Table 68
Migration and Attenuation of Ammonia (as NH₃) in Simulating Dredged
 Material Disposal to Upland Areas - Phase II
 (all values in ppm)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | Sampling Date | | |
|------------------|--|---|---------------|--------------|--------------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Interstitial Water | 1.56 | 0.13 0.16 | 0.17 0.20 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 0.75 | 0.03 | 0.10 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 0.13 | 0.03 | 0.11 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | | | 0.02 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | | 0.04 | 0.06 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | | 0.05 | 0.09 |

Table 69
Migration and Attenuation of Total Kjeldahl Nitrogen in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|--|-------------------------|---------------|---------|--------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction | | 8.9 | 48.3 |
| | | Interstitial Water | 12.6 | 13.1 | 12.1 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 11.0 | 25.5 | 33.4 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 21.0 | 30.2 | 33.8 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | | | 4.5 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | | 22.9 | 4.6 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | | 27.3 | 21.3 |

Table 70
Migration and Attenuation of Nitrate-Nitrogen in Simulating Dredged
Material Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | 6/6/77 | 7/16/77 | 9/7/77 |
|---------------|--|--|--------|--------------|--------------|
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.12 | 0.10 0.16 | 0.17 0.60 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 1.04 | 0.36 | 0.08 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 1.5 | 0.28 | 0.15 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | | 0.13 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.22 | Nil |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | | 0.18 | 0.16 |

Table 71
Migration and Attenuation of Total Phosphorus in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | Sampling Date | |
|---------------|--|-------------------------|---------------|---------|
| | | | 6/6/77 | 7/16/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction | | 0.08 |
| | | Interstitial Water | 0.22 | 0.17 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 0.01 | 0.10 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 0.01 | 0.07 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | | 0.10 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | | 0.10 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | | 0.10 |

Table 72

Migration and Attenuation of Phosphate in Simulating Dredged Material

Disposal to Upland Areas - Phase II

(all values in ppm)

| Column Number | Dredged Material/ Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|---|-------------------------|---------------|---------|--------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction | | 0.01 | 0.08 |
| | | Interstitial Water | 0.22 | 0.17 | 0.11 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 0.01 | 0.05 | 0.30 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 0.01 | 0.03 | 0.02 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | | | 0.03 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | | 0.03 | 0.04 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | | 0.02 | 0.05 |

Table 73
Migration and Attenuation of Sodium in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material/ Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|---|--|----------------------|-------------------|--------------------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 11.5 11.0 2120 | 10 8 1820 | 41 38 3030 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 73 68 1820 | 105 92 2120 | 170 145 2930 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 62 52 2530 | 80 66 2730 | 130 121 3550 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 97 90 2420 | 106 94 2530 | 140 134 3232 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 78 70 2120 | 80 67 2520 | 110 95 3230 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 92 90 2120 | 89 85 2020 | 118 116 3430 |

Table 74
Migration and Attenuation of Potassium in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | 6/6/77 | 7/16/77 | 9/7/77 |
|---------------|--|--|-----------------|-----------------|-----------------|
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 13 12 116 | 18 16 | 48 44 96 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 25 23 91 | 35 32 88 | 54 52 98 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 16 14 139 | 19 19 120 | 44 43 115 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 17 16 121 | 18 14 110 | 34 33 112 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 25 23 111 | 28 25 119 | 51 48 113 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 27 25 101 | 33 30 99 | 46 45 114 |

Table 75
Migration and Attenuation of Calcium in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|--|--|-------------------|------------------|-------------------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 41 40 475 | 71 40 282 | 207 151 202 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 273 162 202 | 141 80 | 353 30 38 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 263 141 283 | 120 66 122 | 298 99 81 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 277 151 323 | 101 40 80 | 281 50 91 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 283 91 303 | 202 82 105 | 212 52 84 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 354 143 202 | 122 55 50 | 280 242 52 |

Table 76

Migration and Attenuation of Magnesium in Simulating Dredged Material
Disposal to Upland Areas - Phase II
 (all values in ppm)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | 6/6/77 | 7/16/77 | 9/7/77 |
|---------------|--|--|-----------------|-------------------|-------------------|
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 11 10 404 | 30 16 353 | 36 32 325 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 80 64 323 | 128 127 328 | 177 161 303 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 53 51 410 | 121 111 404 | 187 138 406 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 81 76 408 | 90 85 373 | 180 171 385 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 81 61 403 | 106 101 404 | 146 139 384 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 96 86 384 | 110 104 368 | 132 131 402 |

Table 77
Migration and Attenuation of Chloride in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|--|-------------------------|---------------|---------|--------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction | | 11000 | 5100 |
| | | Interstitial Water | 4800 | 7200 | 8200 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 5600 | 5100 | 5400 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 7200 | 10800 | 11200 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | | | 180 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | | 130 | 170 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | | 1160 | 1220 |

Table 78
Migration and Attenuation of Iron in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material/ Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|--|---------------------------|---------------|---------|--------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction | 4.7 | 14 | 43 |
| | | Soluble Leachate Fraction | 3.0 | 4 | 0.9 |
| | | Interstitial Water | 0.12 | 0.025 | 0.19 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 0.45 | 0.270 | 8 |
| | | Soluble Leachate Fraction | 0.16 | 0.050 | 0.18 |
| | | Interstitial Water | 0.10 | 0.020 | 0.10 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 0.65 | 2.0 | 6.7 |
| | | Soluble Leachate Fraction | 0.22 | 0.023 | 0.07 |
| | | Interstitial Water | 0.14 | 0.045 | 0.06 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | 0.35 | 0.260 | 1.25 |
| | | Soluble Leachate Fraction | 0.11 | 0.050 | 0.05 |
| | | Interstitial Water | 0.12 | 0.025 | 0.06 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | 0.48 | 0.500 | 3.0 |
| | | Soluble Leachate Fraction | 0.23 | 0.400 | 0.07 |
| | | Interstitial Water | 0.13 | 0.025 | 0.05 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | 0.38 | 0.300 | 0.63 |
| | | Soluble Leachate Fraction | 0.16 | 0.040 | 0.07 |
| | | Interstitial Water | 0.12 | 0.020 | 0.04 |

Table 79
Migration and Attenuation of Manganese in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material/ Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|---|---------------------------|---------------|---------|--------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction | 4.3 | 13.8 | 25 |
| | | Soluble Leachate Fraction | 3.8 | 12.6 | 24 |
| | | Interstitial Water | 0.9 | 0.3 | 0.02 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 1.6 | 3.0 | 6.7 |
| | | Soluble Leachate Fraction | 1.5 | 2.0 | 0.02 |
| | | Interstitial Water | 0.7 | 0.5 | 0.02 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 1.7 | 1.2 | 2.3 |
| | | Soluble Leachate Fraction | 1.5 | 0.5 | 0.02 |
| | | Interstitial Water | 0.5 | 0.1 | 0.02 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | 0.2 | 1.3 | 2.10 |
| | | Soluble Leachate Fraction | 0.2 | 0.9 | 0.02 |
| | | Interstitial Water | 0.6 | 0.1 | 0.03 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | 1.0 | 1.8 | 3.0 |
| | | Soluble Leachate Fraction | 0.5 | 1.6 | 0.02 |
| | | Interstitial Water | 1.3 | 0.2 | 0.02 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | 1.4 | 2.3 | 2.2 |
| | | Soluble Leachate Fraction | 1.2 | 0.6 | 0.08 |
| | | Interstitial Water | 0.4 | 0.2 | 0.02 |

Table 80

Migration and Attenuation of Cadmium in Simulating Dredged Material

Disposal to Upland Areas - Phase II

(all values in ppm)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|--|--|----------------------------|----------------------------|-------------------------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0043 0.0002 0.0015 | 0.0022 0.0008 0.0015 | 0.0003 Nil 0.0004 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0014 0.0001 0.0003 | 0.0020 Nil 0.00035 | 0.0002 Nil 0.0004 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0005 0.0004 0.0007 | 0.0030 Nil Nil | 0.0002 Nil 0.0004 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0007 Nil 0.0005 | 0.0015 Nil 0.0020 | 0.0006 Nil 0.0008 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0016 Nil 0.0004 | 0.0014 Nil 0.0020 | 0.0004 Nil 0.0003 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0007 Nil 0.0004 | 0.0010 Nil 0.0030 | 0.0008 Nil 0.0004 |

Table 81
Migration and Attenuation of Copper in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material/Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|--|--|--------------------------|----------------------------|-------------------------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0006 0.004 0.028 | 0.0075 0.0025 0.0060 | 0.007 0.003 0.007 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.028 0.008 0.018 | 0.0120 0.0060 0.0025 | 0.007 0.003 0.003 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.023 0.008 0.018 | 0.0230 0.0040 0.0035 | 0.020 0.002 0.005 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.042 0.021 0.021 | 0.0140 0.0036 0.0030 | 0.018 0.002 0.003 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.017 0.012 0.018 | 0.022 0.0036 0.0020 | 0.008 0.002 0.002 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.023 0.014 0.016 | 0.0090 0.0030 0.0175 | 0.006 0.002 0.002 |

Table 82
Migration and Attenuation of Mercury in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | 6/6/77 | 7/16/77 | 9/7/77 |
|---------------|--|--|-------------------------|-------------------------|-------------------------|
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0010 0.0004 N11 | 0.0024 0.0003 N11 | 0.0005 0.0004 N11 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.002 N11 N11 | 0.0070 N11 N11 | 0.0065 N11 N11 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0012 N11 N11 | 0.0026 N11 N11 | 0.0030 N11 N11 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0012 0.0001 N11 | 0.0023 N11 N11 | 0.0025 N11 N11 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.0013 N11 N11 | 0.0047 N11 N11 | 0.0040 N11 N11 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.002 N11 N11 | 0.0028 N11 N11 | 0.0030 N11 N11 |

Table 83
Migration and Attenuation of Lead in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|--|--|-------------------------|-------------------------|----------------------------|
| | | | 6/6/77 | 7/16/77 | 9/1/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.007 0.001 0.008 | 0.014 0.003 0.016 | 0.0046 0.0016 0.0060 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.007 0.001 0.009 | 0.013 0.001 0.014 | 0.0050 0.0010 0.0050 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.006 0.001 0.008 | 0.018 0.003 0.018 | 0.0048 0.0008 0.0090 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.005 0.001 0.012 | 0.012 0.002 0.018 | 0.0030 0.0005 0.0080 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.006 0.001 0.011 | 0.008 0.002 0.022 | 0.0020 0.0006 0.0090 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.008 0.001 0.011 | 0.021 0.002 0.020 | 0.0030 0.0005 0.0100 |

Table 84
Migration and Attenuation of Zinc in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in ppm)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|--|--|----------------------|-------------------------|--------------------------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.25 0.23 0.04 | 0.104 0.024 0.003 | 0.150 0.0175 0.005 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.22 0.17 0.08 | 0.020 0.002 0.002 | 0.049 0.003 0.004 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.27 0.13 0.07 | 0.070 0.002 0.002 | 0.018 0.003 0.002 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.16 0.03 0.07 | 0.024 0.004 0.003 | 0.103 0.004 0.001 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.20 0.07 0.03 | 0.015 0.004 0.002 | 0.047 0.003 0.003 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction Soluble Leachate Fraction Interstitial Water | 0.21 0.03 0.03 | 0.023 0.003 0.002 | 0.031 0.002 0.003 |

Table 85
Migration and Attenuation of Chlorinated Pesticides
in Simulating Dredged Material Disposal to Upland Areas - Phase II
(all values in ppb)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | 6/6/77 | 7/16/77 | 9/7/77 |
|---------------|--|-------------------------|--------|---------|--------|
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction | N.D.* | 0.2 | N.D.* |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | | N.D.* | N.D.* |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 0.5 | N.D.* | N.D.* |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | N.D.* | | N.D.* |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | | 0.2 | N.D.* |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | N.D.* | N.D.* | N.D.* |

*Not detectable.

Table 86
Migration and Attenuation of Polychlorinated Biphenyls (as Aroclor
in Simulating Dredged Material Disposal to Upland Areas - Phase II
(all values in ppb)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | 6/6/77 | 7/16/77 | 9/7/77 |
|---------------|--|-------------------------|--------|---------|--------|
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction | N.D.* | N.D.* | N.D.* |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | | N.D.* | N.D.* |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | N.D.* | N.D.* | N.D.* |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | | | N.D.* |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | | N.D.* | N.D.* |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | | N.D.* | N.D.* |

*Not detectable.

Table 87
Migration and Attenuation of Conductivity in Simulating Dredged Material
Disposal to Upland Areas - Phase II
(all values in $\mu\text{S}/\text{cm}$)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | Sampling Date | | |
|---------------|--|-------------------------|--------------------|--------------------|--------------------|
| | | | 6/6/77 | 7/16/77 | 9/7/77 |
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction | | 0.08×10^4 | 0.12×10^4 |
| | | Interstitial Water | 1.11×10^4 | 1.02×10^4 | 1.11×10^4 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 0.12×10^4 | 0.15×10^4 | 0.19×10^4 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 0.13×10^4 | 0.14×10^4 | 0.16×10^4 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | | | 0.17×10^4 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate | | 0.13×10^4 | 0.15×10^4 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | | 0.15×10^4 | 0.14×10^4 |

Table 88
Migration and Attenuation of Oil & Grease in Simulating Dredged Material
Disposal to Upland Areas - Phase II
 (all values in ppm)

| Column Number | Dredged Material / Interfacing Soil | Sample Type | 6/6/77 | 7/16/77 | 9/7/77 |
|---------------|--|-------------------------|--------|---------|--------|
| 11 | Houston/Lake Arrowhead (Acid Rainfall Simulation) | Total Leachate Fraction | | 316 | 17.4 |
| 12 | Houston/Perkins Loam (Rainfall Simulation) | Total Leachate Fraction | 198 | 17.4 | 5.5 |
| 13 | Houston/Perkins Loam (Municipal Leachate Simulation) | Total Leachate Fraction | 380 | 45 | 23.9 |
| 14 | Houston/Perkins Loam (Fulvic Acid Leaching) | Total Leachate Fraction | | | 23.1 |
| 15 | Houston/Perkins Loam (Groundwater Simulation) | Total Leachate Fraction | | 421 | 23.3 |
| 16 | Houston/Perkins Loam (Acid Rainfall Simulation) | Total Leachate Fraction | | 5.6 | 6.9 |
| | | | | | 129.5 |

Table 89
Average Flow Rates of Lysimeter Columns

| <u>Lysimeter Column Number</u> | <u>Dredged Material</u> | <u>Interfacing Soil</u> | <u>Average Flow Rate (ml/d)</u> |
|------------------------------------|-----------------------------|------------------------------|---|
| 1 | Mobile | Lake Arrowhead Sandy Loam | 21.7 |
| 2 | Sayerville | Lake Arrowhead Sandy Loam | 26.2 |
| 3 | Seattle | Lake Arrowhead Sandy Loam | 39.2 |
| 4 | Grand Haven | Lake Arrowhead Sandy Loam | 41.8 |
| 5 | Grand Haven | Lake Arrowhead Sandy Loam | 69.3 |
| 6 | Sayerville | Perkins Loam | 19.4 |
| 7 | -- | Lake Arrowhead Sandy Loam | 41.7 |
| 8 | Seattle | Perkins Loam | 27.5 |
| 9 | Grand Haven | Perkins Loam | 74.1 |
| 10 | -- | Perkins Loam | 46.3 |
| 11 | Houston | Lake Arrowhead Sandy Loam | 22.3 |
| 12 | Houston | Perkins Loam | 21.6 |
| 13 | Houston | Perkins Loam | 18.4 |
| 14 | Houston | Perkins Loam | 16.9 |
| 15 | Houston | Perkins Loam | 17.4 |
| 16 | Houston | Perkins Loam | 19.6 |

Table 90
Oxidation States of Dredged Material
and Interfacing Soils

| <u>Dredged Material</u> | <u>Oxidation State</u> |
|-------------------------|------------------------|
| Houston | Reducing |
| Grand Haven | Oxidizing |
| Seattle | Reducing |
| Sayerville | Reducing |
| Mobile | Slightly oxidizing |
| Lake Arrowhead | Oxidizing |
| Sandy Loam | |
| Perkins Loam | Oxidizing |

Table 91
Typical Leachate Colors

| <u>Lysimeter Column Number</u> | <u>Leachate Color</u> |
|------------------------------------|------------------------|
| 1 | light-amber |
| 2 | amber |
| 3 | light-yellow |
| 4 | amber |
| 5 | amber |
| 6 | yellow |
| 7 | light-amber |
| 8 | yellow |
| 9 | light-yellow to yellow |
| 10 | light-amber to amber |
| 11 | light-brown |
| 12 | yellow |
| 13 | light-brown to brown |
| 14 | amber |
| 15 | light-yellow to yellow |
| 16 | amber |

Table 92
Dredged Material Leachate Constituent Concentrations
and Water-Quality Criteria

| Parameter | Total Concentration | | | | | | Soluble Concentration | | | | | | Public Water Supply Criteria | | |
|--|-----------------------------|-------------------|--------------|-------------------------|---------------|---------------|-----------------------------|-------------------|--------------|-------------------------|---------------|---------------|--------------------------------|-----------------------|------------------------|
| | Freshwater Dredged Material | | | Saline Dredged Material | | | Freshwater Dredged Material | | | Saline Dredged Material | | | EPA Drinking Water Regulations | NAS Proposed Criteria | NTAC Proposed Criteria |
| | (Grand Haven) Ave | (Grand Haven) Max | (Mobile) Ave | (Saverville) Ave | (Seattle) Ave | (Seattle) Max | (Grand Haven) Ave | (Grand Haven) Max | (Mobile) Ave | (Saverville) Ave | (Seattle) Ave | (Seattle) Max | | | |
| pH | — | — | — | — | — | — | 7.1 | 7.2 | 6.8 | 7.2 | 7.2 | 8.1 | 6.5-8.5* | 5-9 | 6-8.5 |
| TOC (ppm) | 318 | 660 | 318 | 430 | 407 | 900 | 251 | 650 | — | 414 | 770 | 436 | — | — | — |
| Alkalinity (ppm as CaCO ₃) | — | — | — | — | — | — | 754 | 1868 | — | — | — | — | — | — | — |
| NO ₃ -N (ppm) | — | — | — | — | — | — | 1.9 | 4.3 | — | — | — | — | — | — | — |
| TKN (ppm) | 27 | 44.7 | 37.6 | 56 | 36 | 71.5 | 27 | 40 | 32.6 | 35 | 49 | 49 | — | — | — |
| NO ₂ -N (ppm) | — | — | — | — | — | — | 12.2 | 30.8 | — | — | — | — | — | — | — |
| Ortho-P (ppm) | 0.05 | 0.16 | 0.04 | 0.05 | 0.07 | 0.34 | 0.03 | 0.11 | <0.01 | 0.01 | 0.02 | 0.02 | 0.1* | 0.1 | 0.1 |
| Cd (ppb) | 3.6 | 4.1 | 8 | 5.2 | 13 | 30 | 2 | — | 3.9 | 8 | 4.4 | 6.5 | 100† | 100 | 100 |
| Cu (ppb) | 52 | 360 | 7.9 | 340 | 67 | 230 | 4.5 | 10 | 5.5 | 12 | 5.7 | 15 | 1000* | 1000 | 1000 |
| Fe (ppm) | 37.7 | 66 | 40.8 | 115 | 48.7 | 135 | 5.8 | 23 | 8.7 | 18 | 4.4 | 35 | 0.3* | 0.3 | 0.3 |
| Hg (ppb) | 6.2 | 33 | 7.7 | 23.7 | 11.2 | 24 | 0.83 | 2.5 | 0.28 | 0.5 | 1.0 | 3 | 2* | 2 | — |
| Mn (ppm) | 16.1 | 31 | 61.5 | 127 | 37.7 | 136 | 13.3 | 30 | 61 | 120 | 37 | 121 | 0.05* | 0.05 | 0.05 |
| Pb (ppb) | 21.9 | 90 | 23.8 | 60 | 35.3 | 110 | 5.7 | 11 | 15.6 | 44 | 21 | 58 | 50* | 50 | 50 |
| Zn (ppb) | 176 | 280 | 665 | 2240 | 238 | 430 | 71 | 180 | 179 | 250 | 138 | 340 | 5000* | 5000 | 5000 |

* EPA National Interim Primary Drinking Water Regulations.

† EPA National Secondary Drinking Water Regulations.

+ Proposed water quality criteria for public supply

o ML = No limit.

(Continued)

Table 92

(Concluded)

| Parameter | Freshwater (Aquatic Life) Criteria | | | Agricultural Water (Irrigation) Criteria | | | Marine Water (Aquatic Life) Criteria | | | Groundwater Contaminant Limits | | | |
|--|---------------------------------------|--|---|--|--|--|--|---|---------------------------------|---|---------------------------------|----------------------------------|---|
| | EPA | NAS | NTAC | EPA | NAS | NTAC | EPA | NAS | NTAC | State of California 50% of 10% of Time | State of New York Schedule I | State of New York Schedule II | State of Missouri Maximum Value Allowed* |
| pH | 6-9 | 6-9 | 6-9 | 4.5-9 | 4.5-9 | 4.5-9 | 6.5-8.5 | 6.5-8.5 | 6.5-8.5 | <0.2 units change | 6.5-8.5 | 6.5-8.5 | — |
| TOC (ppm) | — | — | — | — | — | — | — | — | — | — | — | — | — |
| Alkalinity (ppm as CaCO ₃) | 75% of nature | 75% of nature | ≥20 | — | — | — | — | — | — | — | — | — | — |
| TH ₃ -N (ppm) | 0.02 | EPA | low through bioassay | — | — | — | 0.4 | 0.4 | $\frac{1}{20}$ LC ₅₀ | — | — | — | — |
| TKN (ppm) | — | — | — | — | — | — | — | — | — | — | — | — | — |
| NO ₃ ⁻ -N (ppm) | — | Maintain NO ₃ ⁻ -P ratio | — | — | NL | — | — | — | — | — | 20 | 10 | 10 |
| Ortho-P (ppm) | — | — | — | — | — | — | 0.01 | 0.01 | — | — | — | — | — |
| Cd (ppb) | $\frac{30}{10}$ f $\frac{4}{10}$ * | $\frac{30}{10}$ f $\frac{4}{10}$ * | $\frac{1}{10}$ TL _m $\frac{30}{10}$ | $\frac{10}{5000}$ (20 yr) $\frac{30}{5000}$ (20 yr) $\frac{100}{5000}$ (20 yr) | $\frac{10}{5000}$ (20 yr) $\frac{30}{5000}$ (20 yr) $\frac{100}{5000}$ (20 yr) | $\frac{30}{5000}$ (20 yr) $\frac{100}{5000}$ (20 yr) $\frac{30000}{5000}$ (20 yr) | 100 $\frac{1}{100}$ LC ₅₀ 100 | 10 $\frac{1}{100}$ LC ₅₀ 100 | — | 20 200 200 | 20 400 600 | 10 200 300 | 10 20 — |
| Cu (ppb) | $\frac{10}{10}$ LC ₅₀ | $\frac{10}{10}$ LC ₅₀ | $\frac{10}{10}$ TL _m | $\frac{5}{20}$ (20 yr) $\frac{5}{20}$ (20 yr) $\frac{5}{20}$ (20 yr) | $\frac{5}{20}$ (20 yr) $\frac{5}{20}$ (20 yr) $\frac{5}{20}$ (20 yr) | — | 100 100 100 | 0.3 100 100 | — | — | — | — | — |
| Fe (ppm) | — | — | — | — | — | — | — | — | — | — | — | — | — |
| Hg (ppb) | 200 | 200 | — | — | — | — | 100 | 100 | — | 1 | — | — | — |
| Mn (ppm) | — | — | — | $\frac{0.7}{1000}$ (20 yr) $\frac{10}{1000}$ (20 yr) $\frac{10000}{1000}$ (20 yr) | $\frac{0.7}{1000}$ (20 yr) $\frac{10}{1000}$ (20 yr) $\frac{10000}{1000}$ (20 yr) | $\frac{0.7}{1000}$ (20 yr) $\frac{10}{1000}$ (20 yr) $\frac{10000}{1000}$ (20 yr) | 0.1 $\frac{1}{50}$ LC ₅₀ 100 | 0.1 $\frac{1}{50}$ LC ₅₀ 100 | — | — | 600 100 600 | 300 50 300 | — 50 100 |
| Pb (ppb) | 30 | 30 | — | $\frac{10000}{1000}$ (20 yr) $\frac{10000}{1000}$ (20 yr) $\frac{10000}{1000}$ (20 yr) | $\frac{10000}{1000}$ (20 yr) $\frac{10000}{1000}$ (20 yr) $\frac{10000}{1000}$ (20 yr) | $\frac{10000}{1000}$ (20 yr) $\frac{10000}{1000}$ (20 yr) $\frac{10000}{1000}$ (20 yr) | $\frac{1}{50}$ LC ₅₀ 200 100 | $\frac{1}{50}$ LC ₅₀ 200 100 | — | 100 300 300 | 100 600 600 | 50 300 300 | 50 100 100 |
| Zn (ppb) | $\frac{5}{1000}$ LC ₅₀ | $\frac{5}{1000}$ LC ₅₀ | $\frac{1}{100}$ LC ₅₀ | — | — | — | 200 | 200 | — | 300 500 500 | 600 600 600 | 300 300 300 | 100 100 100 |

f Hard water, all organisms.

* Soft water, all organisms.

* For heavy metals: (in ppb) = $\frac{Cu}{20} + \frac{Zn}{100} + \frac{Pb}{50} + \frac{Cr}{500} + \frac{Cd}{30} + \frac{Ni}{800} \leq 1.00$

Table 93
Impact Potentials of Dredged Material Leachates

| Parameter | Lake Arrowhead Sandy Loam | | | Perkins Loam | | |
|---------------------------------|---------------------------|--------------------------|-----------------|------------------------|--------------------------|-----------------|
| | Mobi- lity Index | Evalua- tory Index | Impact Index | Mobi- lity Index | Evalua- tory Index | Impact Index |
| | (MI) | (EI) | (II) | (MI) | (EI) | (II) |
| TOC | 1.93 | 377 | 727 | 1.86 | 411 | 765 |
| NH ₃ -N | 0.46 | 0.92 | 0.42 | 0.62 | 1.25 | 0.78 |
| TKN | 1.34 | 46.6 | 62.5 | 1.23 | 102 | 126 |
| NO ₃ ⁻ -N | 30.9 | 0.75 | 23.2 | 20.4 | 0.93 | 19.0 |
| Total-P | 21.6 | 5.36 | 116 | 20.4 | 21.4 | 437 |
| Ortho-P | 2.41 | 0.35 | 0.83 | 1.78 | 0.26 | 0.46 |
| Na ⁺ | 0.34 | 4.48 | 1.53 | 1.03 | 2.67 | 2.74 |
| K ⁺ | 0.99 | 0.54 | 0.54 | 1.47 | 0.60 | 0.88 |
| Ca ²⁺ | 3.70 | 1.93 | 7.13 | 2.77 | 2.40 | 6.64 |
| Mg ²⁺ | 0.37 | 0.42 | 0.15 | 1.80 | 1.03 | 1.86 |
| Cl ⁻ | 0.87 | 10.9 | 9.50 | 1.71 | 8.48 | 14.5 |
| Cd | 0.36 | 0.076 | 0.027 | 0.339 | 0.057 | 0.019 |
| Cu | 0.77 | 0.008 | 0.006 | 0.89 | 0.016 | 0.015 |
| Fe | 32.0 | 51.7 | 1650 | 1.05 | 1.92 | 2.02 |
| Hg | 1.28 | 0.37 | 0.47 | 1.12 | 0.57 | 0.63 |
| Pb | 0.46 | 1.49 | 0.69 | 0.25 | 0.63 | 0.16 |
| Mn | 58.7 | 1080 | 63300 | 1.46 | 90.6 | 132 |
| Zn | 2.33 | 0.028 | 0.064 | 0.554 | 0.012 | 0.006 |

Table 94
Relative Ranking of Impact Potentials of
Dredged Material Leachates

| <u>Mobility Index</u> | | <u>Evaluatory Index</u> | | <u>Impact Index Ranking</u> | |
|-----------------------|------|---------------------------------|------|---------------------------------|-------|
| Mn | 30 | Mn | 580 | Mn | 17500 |
| NO ₃ -N | 26 | TOC | 390 | TOC | 748 |
| Total-P | 21 | TKN | 755 | Fe | 442 |
| Fe | 16.5 | Fe | 26.8 | Total-P | 281 |
| Ca ²⁺ | 3 | Total-P | 13.4 | TKN | 96 |
| Ortho-P | 2.1 | Cl ⁻ | 9.7 | NO ₃ ⁻ -N | 22 |
| TOC | 1.9 | Ca ²⁺ | 2.2 | Cl ⁻ | 12 |
| Zn | 1.4 | Na ⁺ | 2.1 | Ca ²⁺ | 7 |
| Cl ⁻ | 1.3 | NH ₃ -N | 1.1 | Na ⁺ | 1.5 |
| TKN | 1.3 | Pb | 1.1 | Mg ²⁺ | 0.8 |
| K ⁺ | 1.2 | NO ₃ ⁻ -N | 0.84 | K ⁺ | 0.7 |
| Hg | 1.2 | Mg ²⁺ | 0.7 | Ortho-P | 0.64 |
| Mg ²⁺ | 1.1 | K ⁺ | 0.6 | NH ₃ -N | 0.60 |
| Cu | 0.8 | Hg | 0.5 | Hg | 0.55 |
| Na ⁺ | 0.7 | Ortho-P | 0.31 | Pb | 0.4 |
| NH ₃ -N | 0.5 | Cd | 0.07 | Zn | 0.03 |
| Pb | 0.4 | Zn | 0.02 | Cd | 0.02 |
| Cd | 0.4 | Cu | 0.01 | Cu | 0.01 |

Table 95

Liner Materials and Characteristics

| Liner Material | Permeability* | Advantages | Longevity** A B C D | Prohibitory Conditions | Other Disadvantages | Comments | References |
|---|---------------------|--|------------------------|--|---|---|------------------------------|
| | | | | | | | |
| A. Compacted natural fine grain soils | $10^{-5} - 10^{-7}$ | Low cost Materials readily available | L S N S | Vegetation | Lack of quality control Easily disrupted by traffic | Could be used with relatively innocuous material and long distances to aquifers or surface water sources. Otherwise, too many unknowns. | 139, 140 |
| B. Natural clays | $10^{-6} - 10^{-8}$ | Lower cost than other clay liners Generally relies on in-place clays | I M N S | Very susceptible to high TDS content Vegetation | Variable quality May contain coarser materials which can interfere with sealant function | Many sites have natural clay layers which provide an effective liner. Natural liners are an unknown, though often of indeterminate thickness and composition. However, they generally require only minimum artificial liners to maintain site impermeability. | 137, 140 |
| C. Bentonite/sand mixtures | 10^{-7} | Swells on water contact to form a water-tight liner Self-healing properties | I M N S | Very hard water Heavy metals High salt content Vegetation | Subject to damage from plant roots, burrowing insects, and animals | Permeabilities increase with decreasing bentonite content. Because of their geochemistry and microcrystalline structure, bentonite clays are susceptible to degradation from high salt or hard waters. | 139, 140, 141, 142, 143, 144 |
| D. Polymer-modified bentonite/sand mixtures | $10^{-7} - 10^{-9}$ | Useful where TDS exceeds 1,000 ppm | I L S S | Vegetation | | The polymer modification enables the bentonite to withstand the chemical attacks which would otherwise prove detrimental to nonmodified bentonite. | 139, 143 |
| E. Soil cement | $10^{-6} - 10^{-8}$ | Low cost | L S N S | Acid dredged material | Lack of homogeneity in liner | Has successfully been used to line many canals, reservoirs, other water-containing structures. | 139, 140, 145, 146, 147 |

*Cal/sec except as noted.

**Expected duration (in years) of impermeable membrane with minimum maintenance:

- A = Freshwater, relatively unpolluted dredged material.
 B = Salt water, relatively unpolluted dredged material.
 C = Dredged material with a high acid, alkali, heavy metal content.
 D = Dredged material with a high organic, hydrocarbon, aromatic content.
 I = Indefinite.
 L = 10 to 25 years.
 M = Not recommended.
 S = <10 years.

(Continued)

*Environmental or dredged material characteristics which could prohibit use of liner.

Table 95

(Continued)

| Liner Material | Permeability ^a | Advantages | Longevity ^{aa} | | | | Prohibitory Conditions | Other Disadvantages | Comments | References |
|---------------------------|---|--|-------------------------|---|---|---|--|--|--|--------------------|
| | | | A | B | C | D | | | | |
| F. Chemical soil sealants | Variable, depending on the sealant, usually 10^{-5} - 10^{-9} | Low cost Ease of application | L | S | N | N | Oily materials Industrial chemicals Vegetation | Lack of control over sealing or polymerization process Little structural strength | Includes sprayed polymers, admixed latexes, carbonate bonding. All work best in fine soils. | 139, 143, 144, 148 |
| G. Concrete | 10^{-6} - 10^{-8} | Longevity Structural strength Not susceptible to damage from burrowing animals | I | L | S | L | Acid materials Alkaline materials Sulfates | High cost Cannot be placed in freezing weather | Concrete has a very long history of successful application as an impermeable liner or water barrier in dams, canals, reservoirs, waste lagoons, buildings, etc. | 140, 143, 145, 146 |
| H. Shotcrete | 10^{-6} | Easily placed over rough grade | L | S | N | S | Acid materials | More costly than regular concrete Difficult to control thickness during application Low resistance to compressive forces | Pneumatically applied concrete is often used as a canal lining. | 140, 146 |
| I. Asphalt concrete | 10^{-5} - 10^{-6} | Easily applied | L | S | N | N | Oily materials | Approximately 5 percent void space | Normal highway concrete. Its high void space greatly increases its permeabilities over other liner materials. It is inexpensive and easy to use. However, and has been used with membranes or clay to line sanitary landfills. | 140, 145 |

(Continued)

Table 95

(Continued)

| Liner Material | Permeability ^a | Advantages | Longevity ^{b,c} A B C D | Prohibitory Conditions ^d | Other Disadvantages | Comments | References |
|--|---------------------------|---|-------------------------------------|--|--|--|-----------------------------------|
| | | | | | | | |
| J. Hydraulic asphalt concrete | $10^{-8} - 10^{-9}$ | Voidless | L S S M | Oily materials | More costly than normal asphalt concrete | A more refined asphalt concrete. It is voidless, but has structural strength, is costly, and is more difficult to install than normal asphalt concrete. | 139, 140, 144 |
| K. Bituminous seals | $10^{-6} - 10^{-8}$ | Easily applied Inexpensive | L S S M | Oily materials Vegetation | Questionable homogeneity of liner Little structural strength | Catalytically blown bituminous seals resemble synthetic membranes in their effect. They have less structural integrity, however. | 140, 143, 145 |
| L. Soil asphalt | $10^{-5} - 10^{-6}$ | Easily applied Inexpensive | S M M M | Oily materials Vegetation | May disintegrate completely in presence of leachate Susceptible to bacteria | Tests with typical leachates have shown rapid disintegration times. Might be acceptable for leachate materials at relatively secure sites. | 140, 144, 145, 149 |
| M. Butyl rubber | 0.0017 Perms ^f | Resistant to animal and vegetable fats and oils | L L S M | Hydrocarbons | Difficult to seam in the field | Widely used as landfill liners. Field installation sometimes difficult because of seaming problems. Field seams are usually the weakest part of the liner. | 139, 143, 145, 150, 151, 152, 153 |
| N. Chlorinated polyethylene (CPE) | 0.028 Perms | High chemical and bacterial resistance | L L S M | Hydrocarbons organic solvents | | | 139, 143, 145, 150, 151, 152, 153 |
| O. Chlorosulfonated polyethylene (Hypalon) | 0.024 Perms | Good puncture resistance Easily seamed in the field Resistant to oil and bacteria Acid resistant | L L L S | Some organic solvents | High cost | Second to PVC in synthetic liner popularity. | 139, 143, 150, 151, 152, 153 |

(Continued)

^fPerms = 10^{-10} m/sec/cm²/mm Hg.

Table 95

(Concluded)

| Liner Material | Permeability ^a | Advantages | Longevity ^{a,b} A B C D | Prohibitory Conditions ^c | Other Disadvantages | Comments | References |
|--|---------------------------|--------------------------------------|-------------------------------------|--|--|---|--|
| | | | | | | | |
| P. Ethylene-propylene diene monomer (EPDM) | 0.015-0.028 Perms | | L L S N | Many hydrocarbons | Difficult to seam in the field | A fairly new liner material, but one with proven potential. Its seam problems can make field installation difficult. | 139, 143, 145, 150, 151, 152, 153 |
| Q. Polychloroprene (neoprene) | 0.008-0.039 Perms | Oil resistant | L S S S | High cost | Difficult to seam in the field | Neoprene is often used in automobile engines because of its oil and grease resistance. | 139, 143, 145, 150, 151, 152, 153 |
| R. Polyethylene (PE) | 0.91 Perms | Biodegradation resistant | L L S N | Rocky silt or dredged material Organic solvents | Tears easily Susceptible to rodent damage May have pinholes, blisters | Has been used successfully to line many landfills, lagoons, dredged material lagoon dikes. Could easily be damaged if heavy equipment used for dredged material conditioning. | 137, 139, 143, 145, 150, 151, 152, 153 |
| S. Polyvinyl chloride (PVC) | 0.16-0.36 Perms | Puncture resistant Easy to splice | L S S N | Organic solvents | Some PVC plasticizers subject to chemical and biological degradation Difficult to install in cold weather | Most popular synthetic liner for water-containing structures and land disposal sites. Careful choice of particular PVC compound needed to ensure a nondegradable membrane. Cannot be exposed to environmental conditions for very long. | 139, 143, 145, 150, 151, 152, 153 |
| T. High silt dredged material | $10^{-7} - 10^{-8}$ | | L L S S | | Lack of quality control | Dredged material often forms seals in disposal lagoons or on dikes. | 137, 138, 149 |

Table 96
Liner Applications

| Site Characteristics | Freshwater Dredged Material* | | | Saltwater Dredged Material | | |
|-----------------------------------|---|---|------------------------|--|--|----------------------------|
| | I** | II | III | I | II | III |
| High Water Table | | | | | | |
| Coarse soils, fractured bed-rocks | C, D, E, G, (H), J, (K), M, N, O, P, Q, R, S | (D), (J), (M), N, O, (P), (Q), (R), (S) | (C), (E), (G), (Q) | (G), (I), (M), N, O, (P), (Q), (R), (S) | (M), N, O, (P), (R) | (G), (Q) |
| Fine Soils A, B | C, D, E, (F), G, H, J, K, (L), M, N, O, P, Q, R, S | D, (E), (G), (H), J, (K), M, N, O, P, Q, (R), S | C, (E), G, (H), (Q), Q | (D), (E), (F), (G), (H), J, (K), M, N, O, (P), (Q), (R), S | (D), (E), (J), (M), N, O, (P), (Q), (R), (S) | (D), (E), (H), (G), (Q), Q |
| Low Water Table | | | | | | |
| Coarse soils, fractured bed-rocks | C, D, E, (F), G, H, J, K, (L), M, N, O, P, Q, R, S | D, (E), G, (H), J, (K), M, N, O, P, Q, (R), S | C, (E), G, (H), (Q), Q | (E), (F), G, (H), J, (K), M, N, O, (P), (Q), (R), S | (J), M, N, P, Q, (R), S | (G), (H), (Q) |
| Fine soils A, B | C, D, E, F, G, H, (I), J, K, L, M, N, O, P, Q, R, S | D, (E), (F), G, H, (I), J, K, M, N, O, P, Q, R, S | C, (E), G, H, O, Q | D, E, F, G, (H), (I), J, K, M, N, O, P, Q, R, S | D, (E), (F), (G), (I), J, (K), M, N, O, P, Q, R, S | D, E, G, (H), O, Q |

*See Table 95 for liner code (letters correspond to liner materials in that table).

Liner codes in parentheses are applicable for fine-grained dredged material or short liner lives only. Other codes are applicable for any of the specified conditions.

**I - Relatively clean dredged material.

II - Dredged material high in sulfur, heavy metal, etc. (e.g., Mobile).

III - Dredged material high in hydrocarbons, aromatics, etc. (e.g., Seattle, Grand Haven).

Table 97
Characteristics of Sanitary Landfill Leachate*

| Characteristic (mg/l) | Site** | | | | | |
|--------------------------|--------|-------|-------------------|---------|--------|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| pH | 5.6 | 5.9 | 8.3 | — | — | — |
| Total hardness as | | | | | | |
| CaCO ₃ | 8,120 | 3,260 | 537 | — | 8,700 | 500 |
| Iron total | 305 | 336 | 219 | 1,000 | — | — |
| Sodium | 1,805 | 350 | 600 | — | — | — |
| Potassium | 1,860 | 655 | N.R. [†] | — | — | — |
| Sulfate | 630 | 1,220 | 99 | — | 940 | 24 |
| Chloride | 2,240 | N.R. | 300 | 2,000 | 1,000 | 220 |
| Nitrate | N.R. | 5 | 18 | — | — | — |
| Alkalinity as | | | | | | |
| CaCO ₂ | 8,100 | 1,710 | 1,290 | — | — | — |
| Ammonia nitrogen | 845 | 141 | N.R. | — | — | — |
| Organic nitrogen | 550 | 152 | N.R. | — | — | — |
| COD | N.R. | 7,130 | N.R. | 750,000 | — | — |
| BOD | 32,400 | 7,050 | N.R. | 720,000 | — | — |
| Total dissolved solids | N.R. | 9,190 | 2,000 | — | 11,254 | 2,075 |

*Ref. 154.

**No age of fill specified for Sites 1 through 3, Site 4 is initial, 5 is 3 yr old, and 6 is from a 15-yr-old fill.

†N.R.: no results.

Table 98
Concentration Ranges of Parameters in Sanitary Landfill Leachate*

| Constituent | Concentration Range |
|-------------------------------|---------------------|
| | (mg/l) |
| Iron | 200-1,700 |
| Zinc | 1-135 |
| Phosphate | 5-130 |
| Sulfate | 25-500 |
| Chloride | 100-2,400 |
| Sodium | 100-3,800 |
| Nitrogen | 20-500 |
| Hardness as CaCO ₃ | 200-5,250 |
| COD | 100-51,000 |
| Total Residue | 1,000-45,000 |
| Nickel | 0.01-0.8 |
| Copper | 0.10-9.0 |
| pH | 4.00-8.5 |

*Ref. 154

Table 99
Summary of Metal Removal by Settling Biological Floc*

| Data | Experiment Number | | | | | |
|--|-------------------|--------|--------|--------|--------|--------|
| | (1) | (2) | (3) | (4) | (5) | (6) |
| Solids Detention Time, in days | 10 | 20 | 30 | 30 | 45 | 60 |
| Steady-State MLSS** Concentration, in parts per million | 24,250 | 22,650 | 20,800 | 19,550 | 20,300 | 14,300 |
| Steady-State MLVSS† Concentration, in parts per million | 16,100 | 15,100 | 13,500 | 10,590 | 11,880 | 8,100 |
| Percentage of Mixed Liquor Metal Concen- trations Removed by Settling Biological Floc: | | | | | | |
| Aluminum | 97.51 | 98.42 | 99.15 | 99.19 | 100 | 100 |
| Cadmium | 96.88 | 97.68 | 98.58 | 97.33 | 97.83 | 98.50 |
| Calcium | 97.99 | 98.52 | 98.27 | 94.85 | 96.11 | 93.53 |
| Chromium | 92.51 | 96.76 | 96.63 | 96.76 | 97.75 | 97.10 |
| Iron | 98.61 | 99.70 | 99.84 | 99.84 | 99.94 | 99.99 |
| Lead | 79.85 | 83.61 | 85.45 | 83.70 | 87.50 | 89.62 |
| Magnesium | 54.57 | 68.51 | 65.16 | 59.71 | 60.65 | 49.22 |
| Manganese | 95.73 | 98.12 | 98.62 | 98.83 | 99.47 | 99.60 |
| Nickel | 70.31 | 71.87 | 81.25 | 75.80 | 75.80 | 85.19 |
| Potassium | 16.67 | 9.72 | 7.58 | 8.60 | 14.11 | 15.18 |
| Zinc | 99.08 | 99.23 | 99.63 | 99.60 | 99.86 | 99.88 |

*Ref. 154.

**MLSS - mixed liquor suspended solids.

†MLVSS - mixed liquor volatile suspended solids.

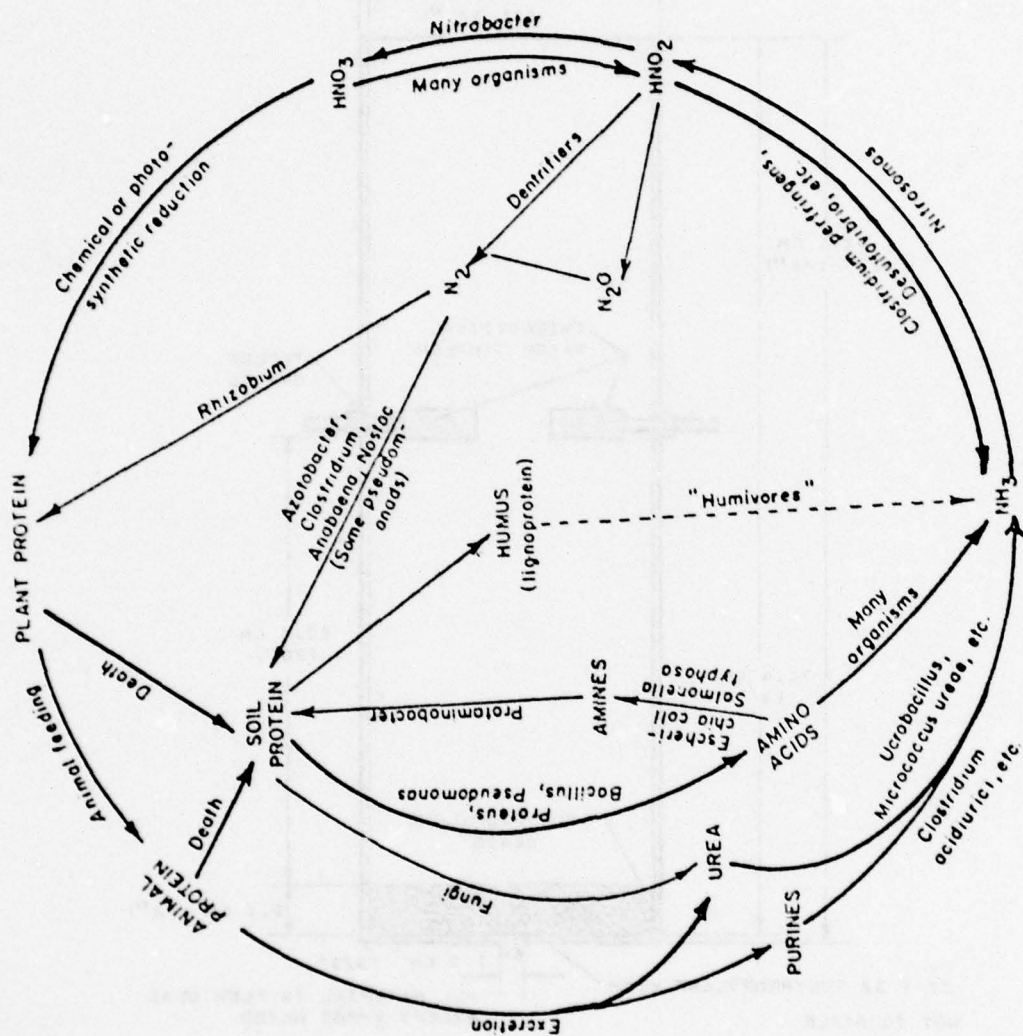


Figure 1. The Nitrogen Cycle in Nature (13).

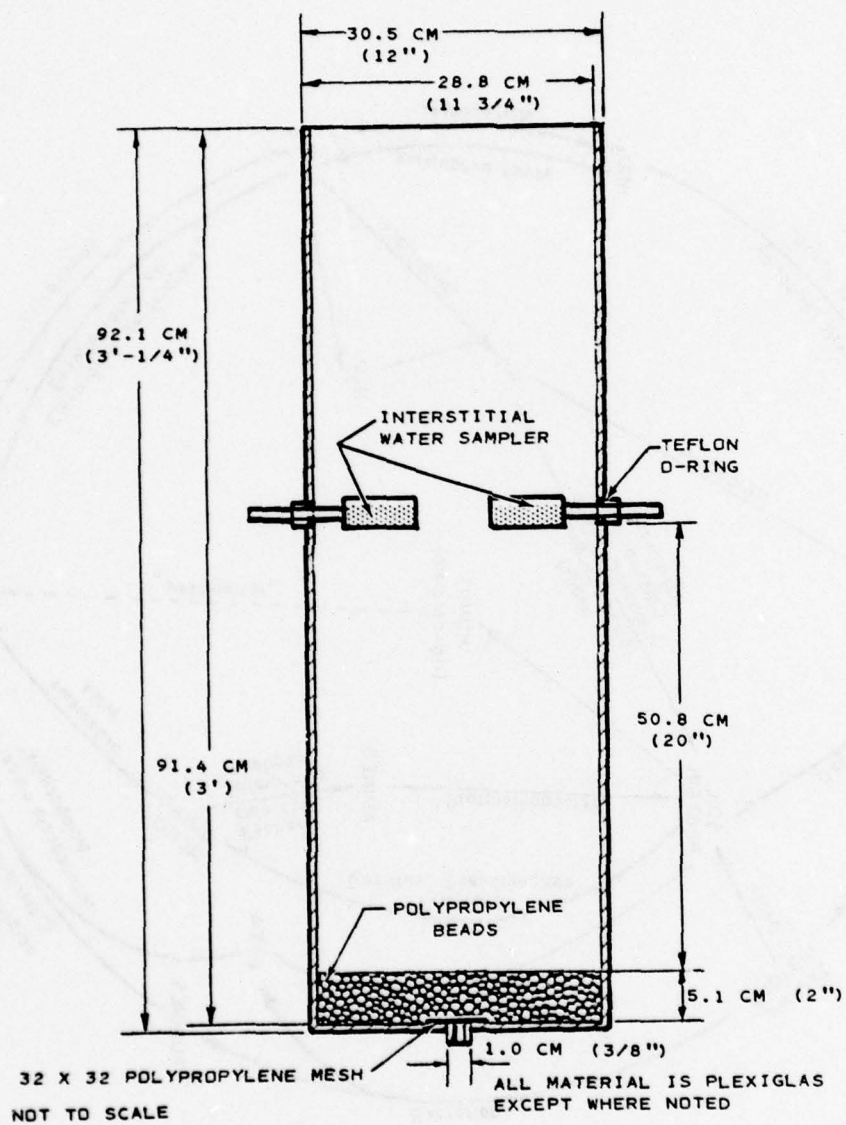


Figure 2. Lysimeter Column.

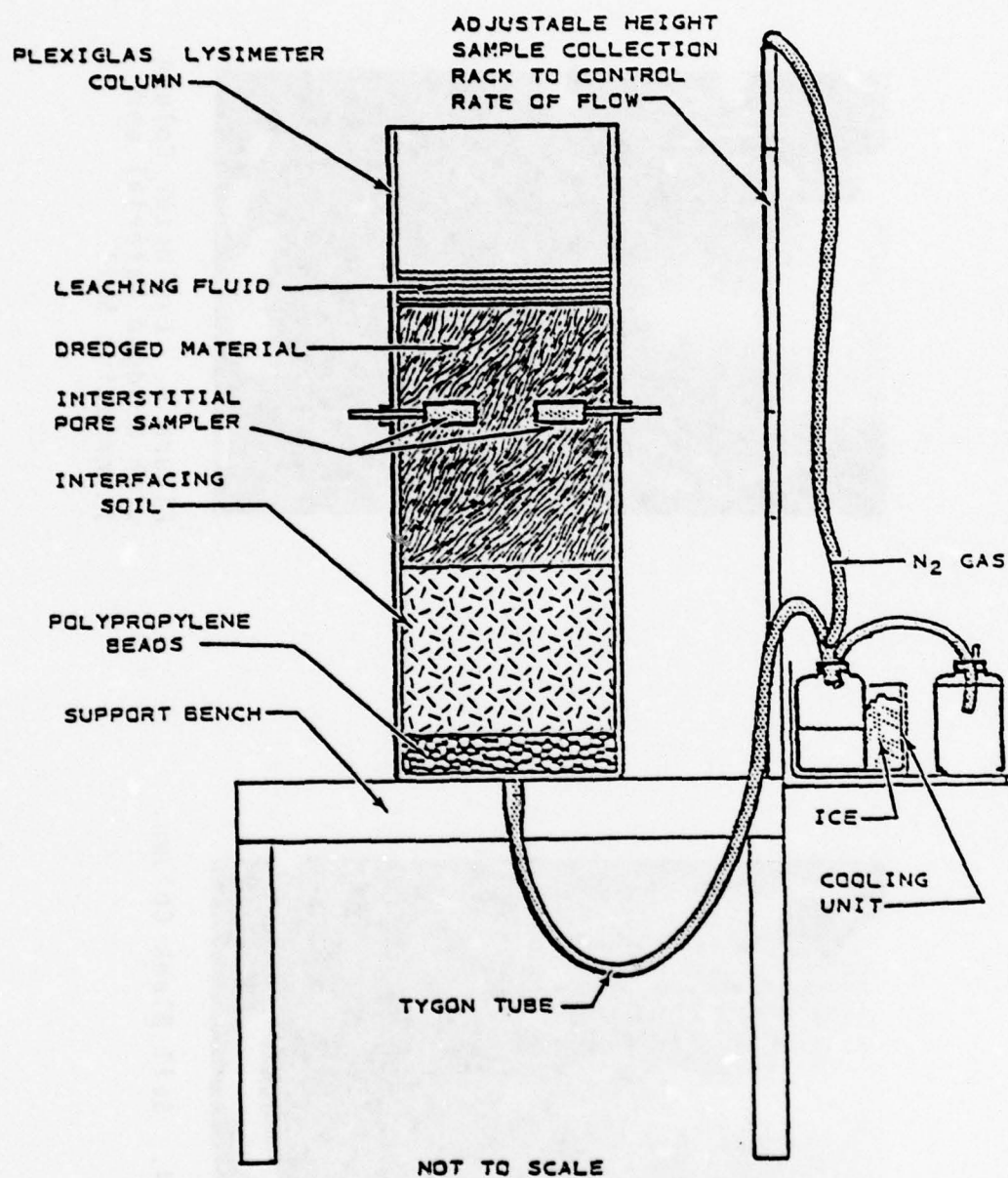


Figure 3. Lysimeter Column Experimental Setup.



Figure 4. Soil Blank Column.



Figure 5. Lysimeter Column with Dredged Material and Interfacing Soil.

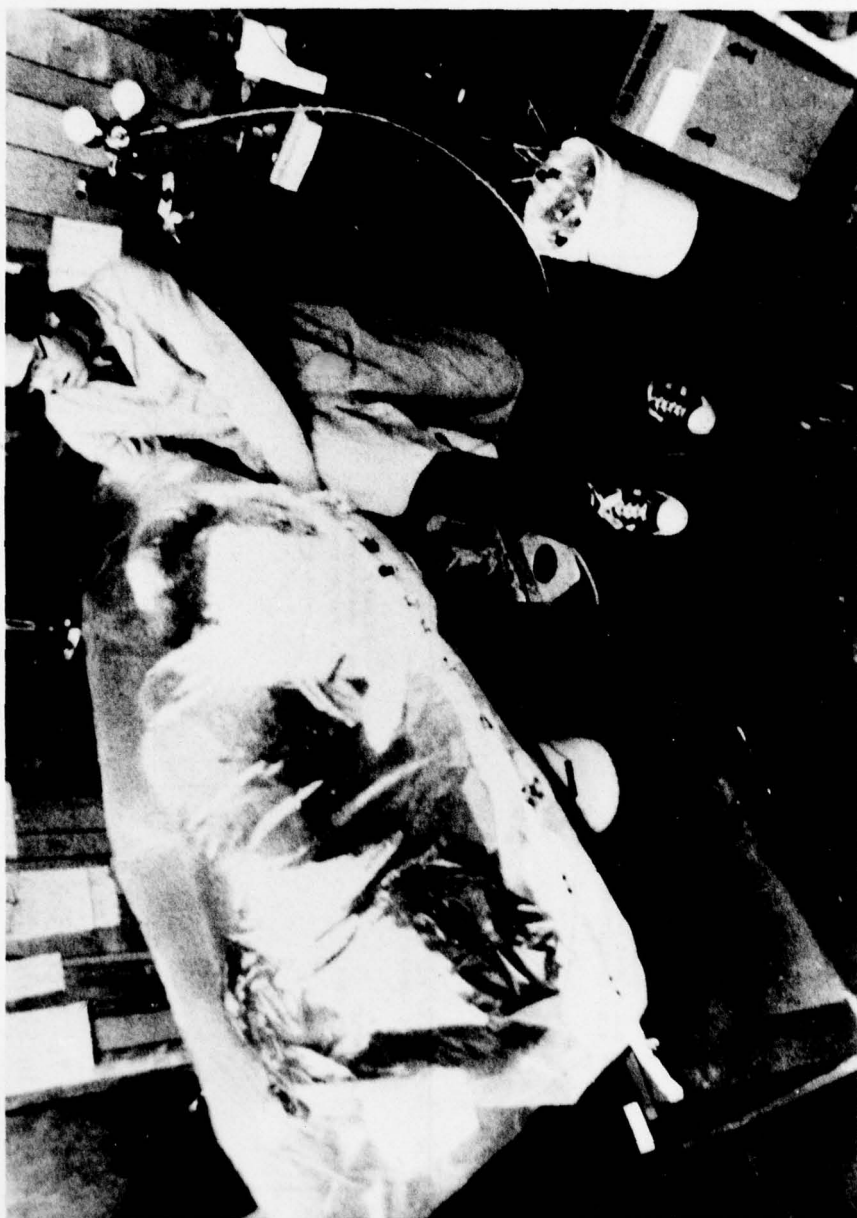


Figure 6. Removal of Interfacing Soils and Dredged Material from Lysimeter Columns.

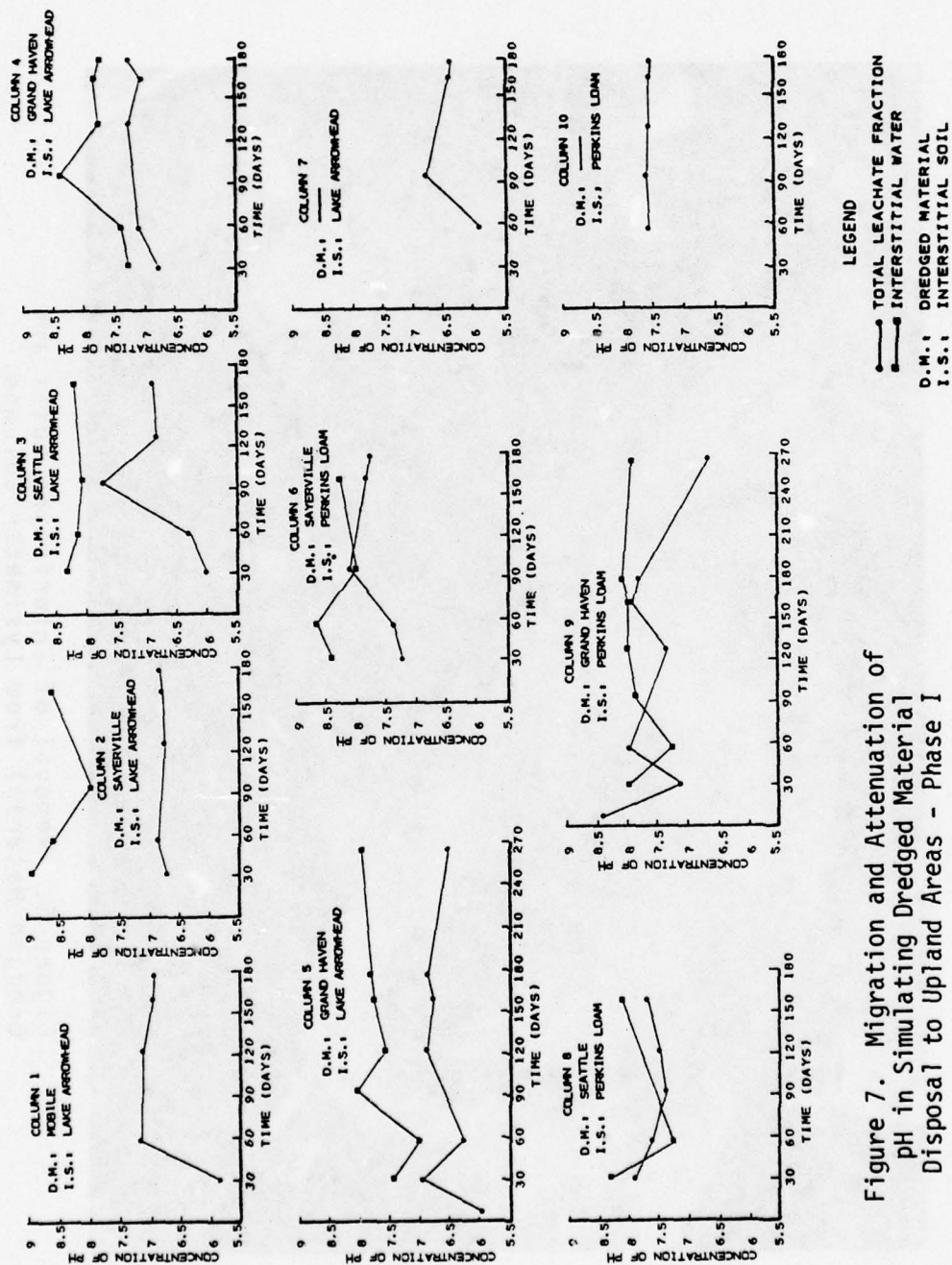


Figure 7. Migration and Attenuation of pH in Simulating Dredged Material Disposal to Upland Areas - Phase I

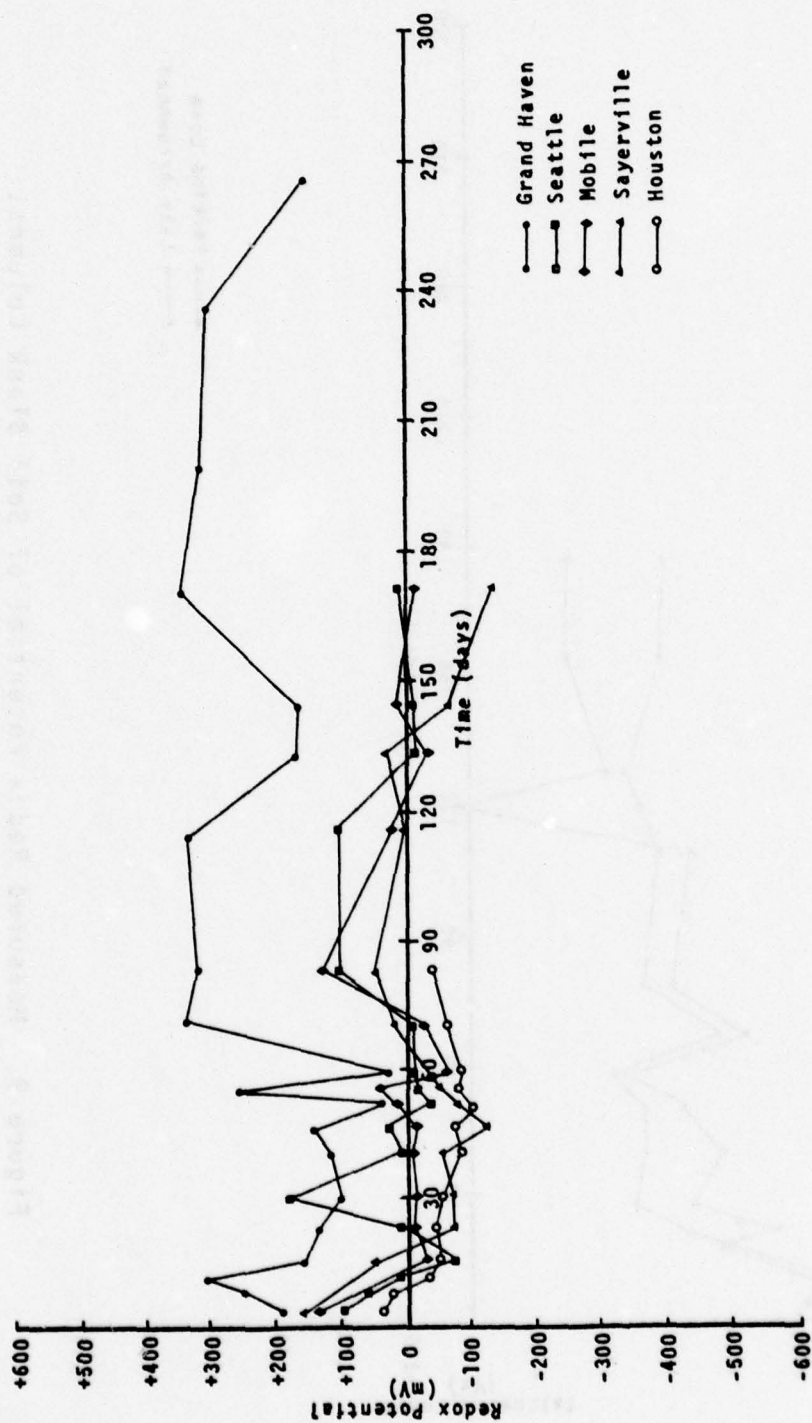


Figure 8. Measured Redox Potential of Dredged Material.

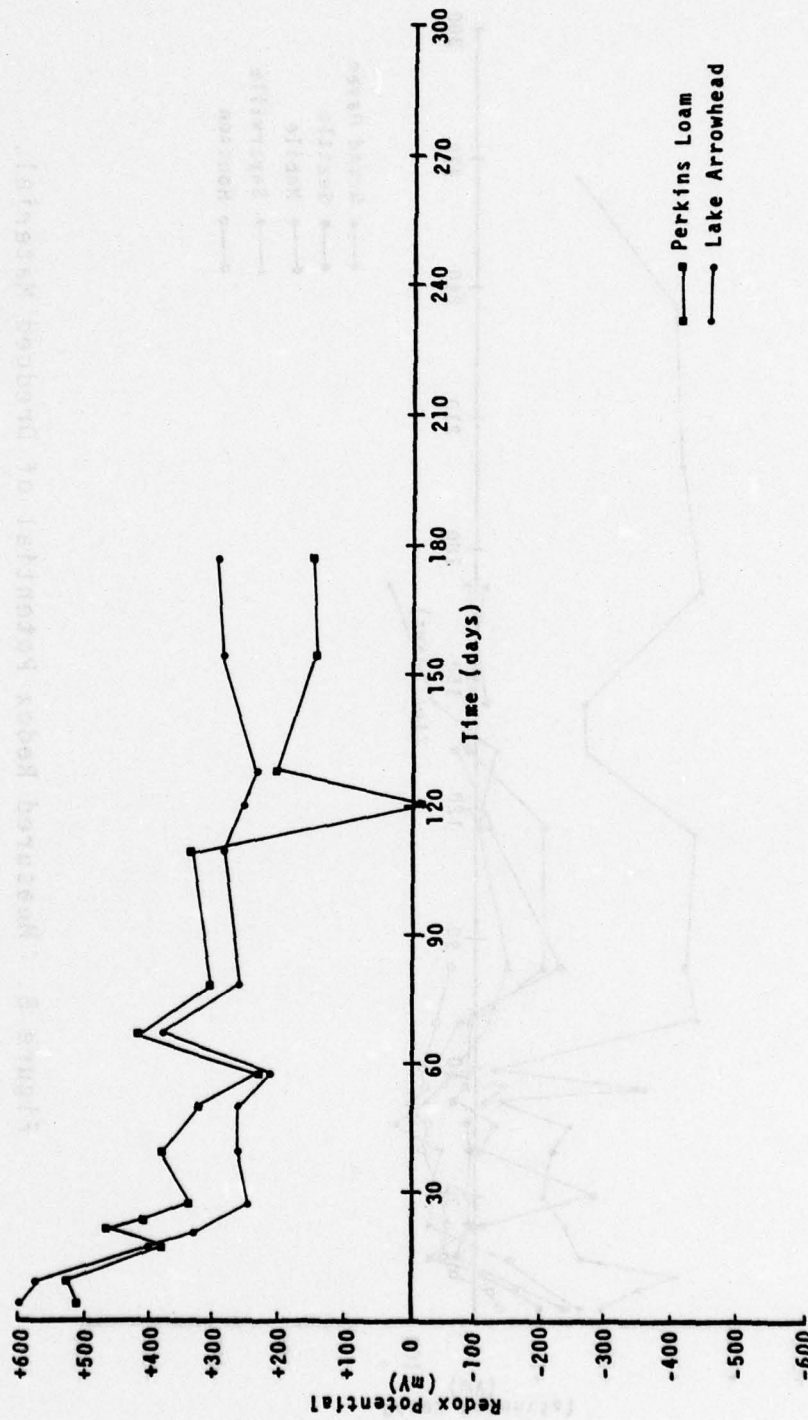


Figure 9. Measured Redox Potential of Soil Blank Columns.

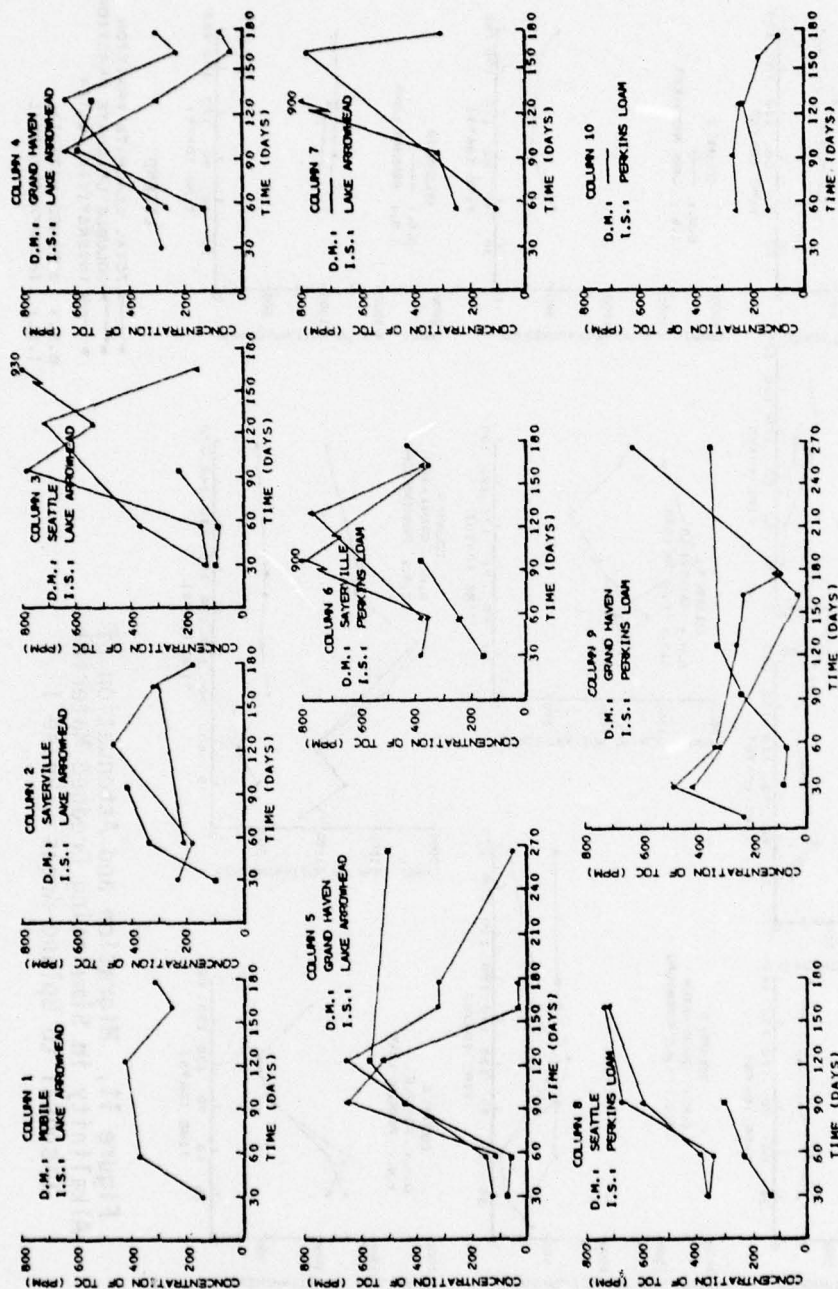


Figure 10. Migration and Attenuation of Total Organic Carbon in Simulating Dredged Material Disposal to Upland Areas - Phase I

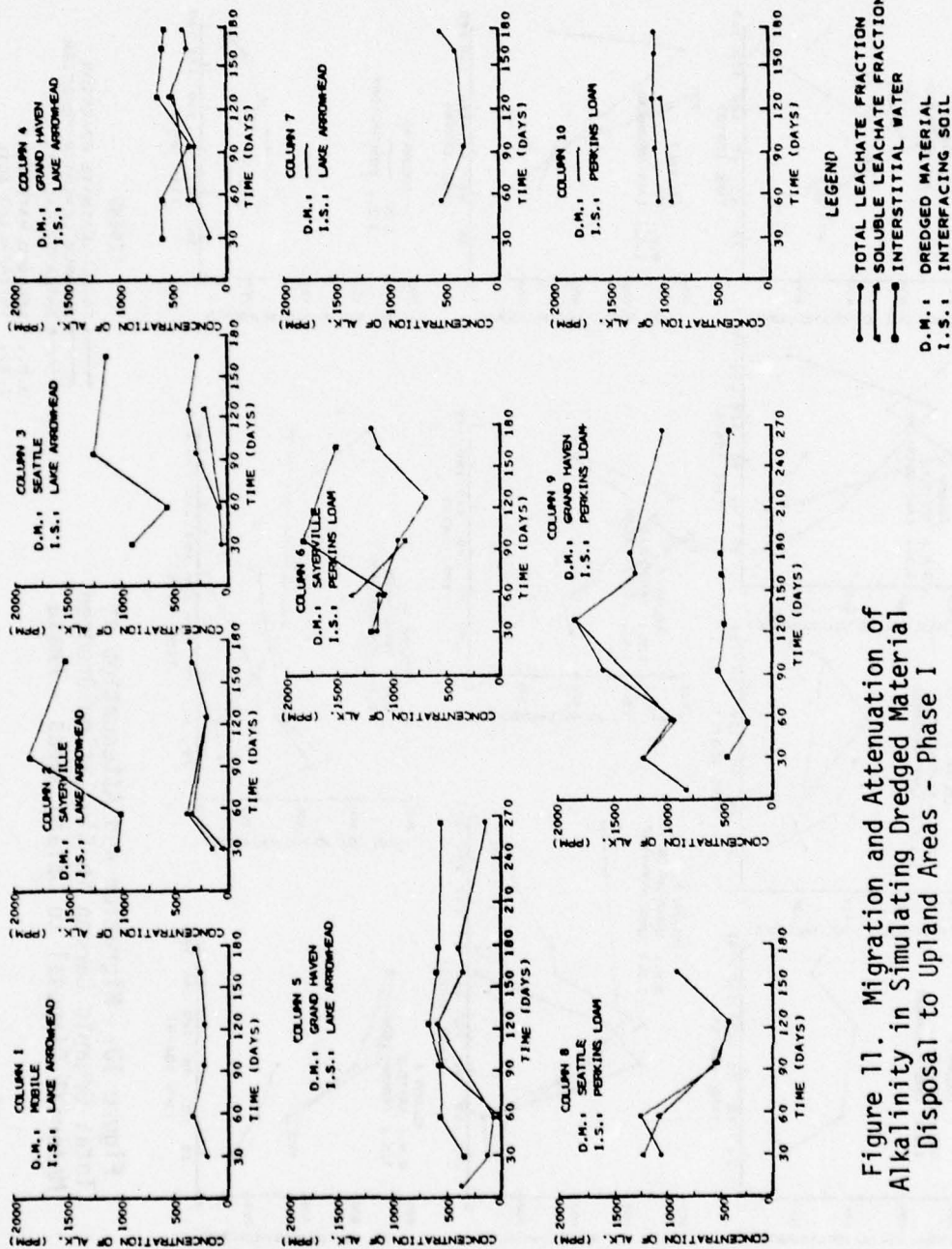


Figure 11. Migration and Attenuation of Alkalinity in Simulating Dredged Material Disposal to Upland Areas - Phase I

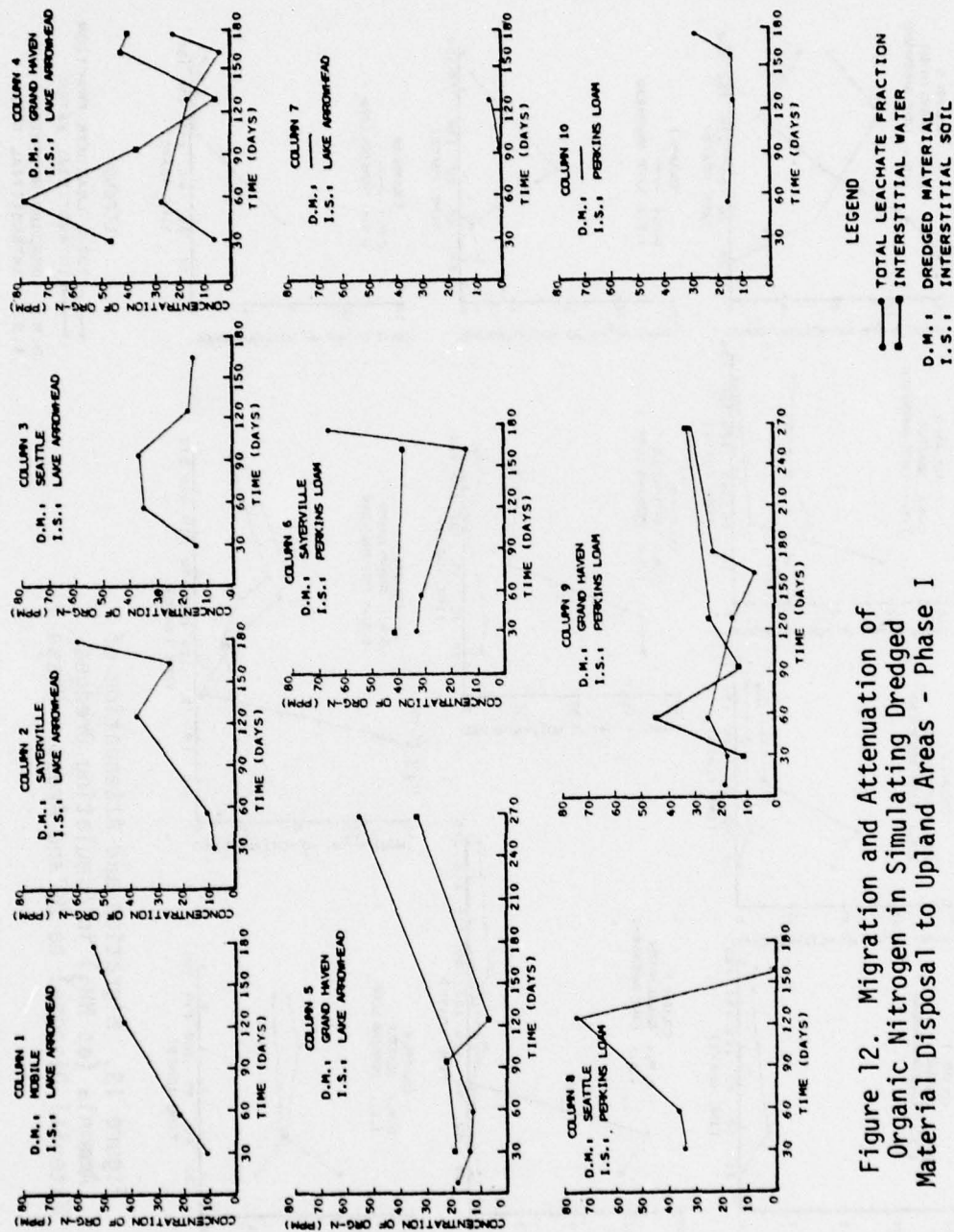


Figure 12. Migration and Attenuation of Organic Nitrogen in Simulating Dredged Material Disposal to Upland Areas - Phase I

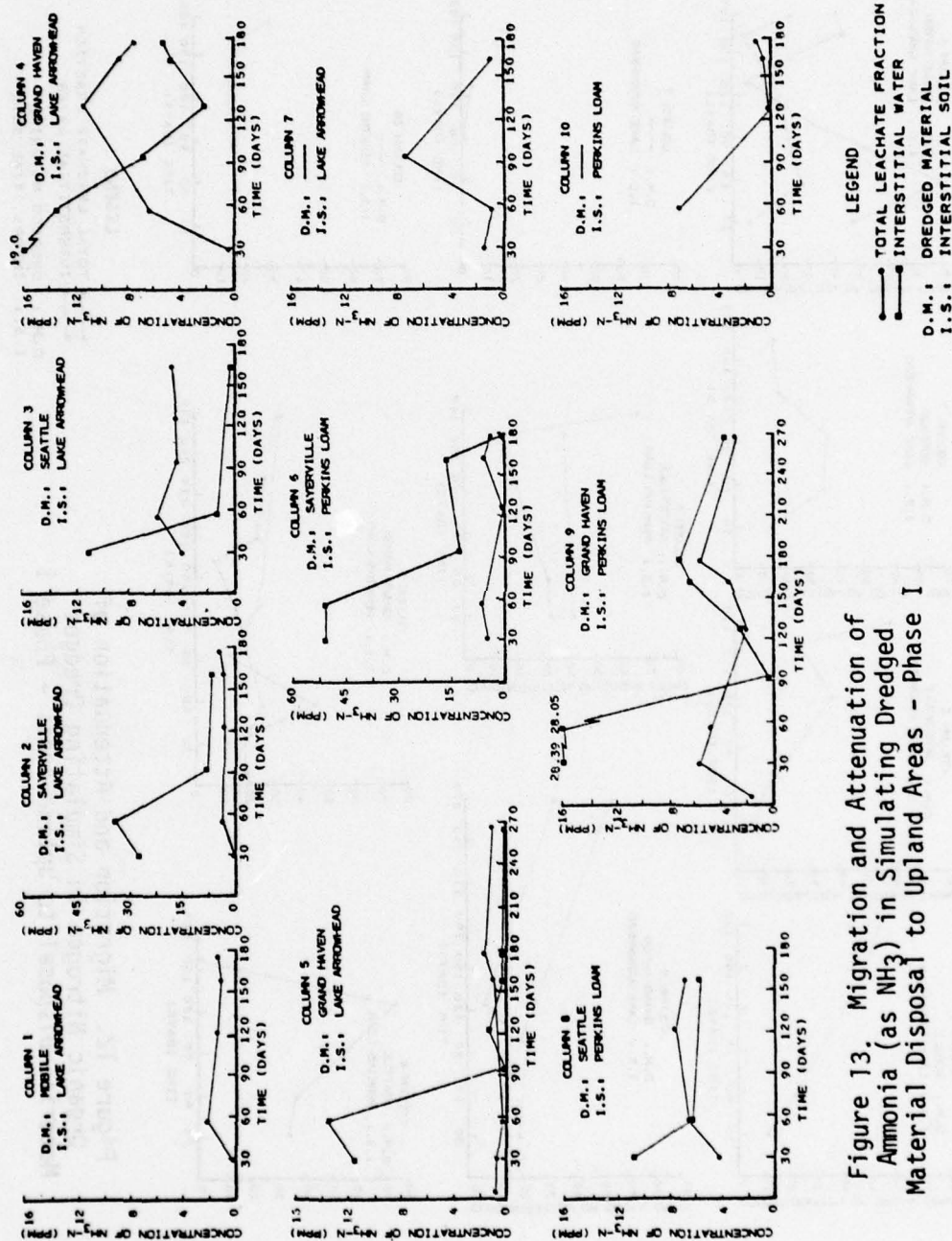


Figure 13. Migration and Attenuation of Ammonia (as NH_3) in Simulating Dredged Material Disposal to Upland Areas - Phase I

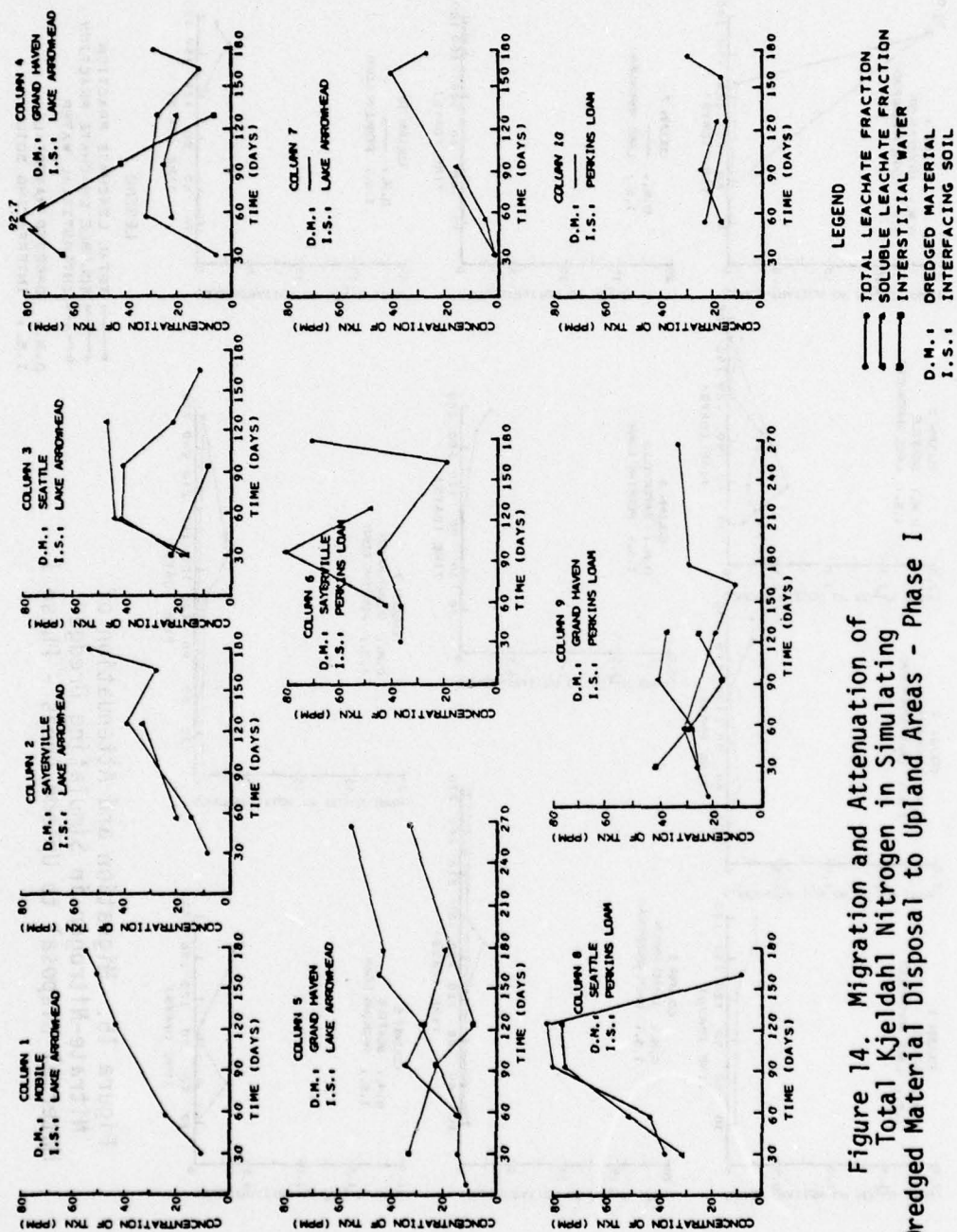
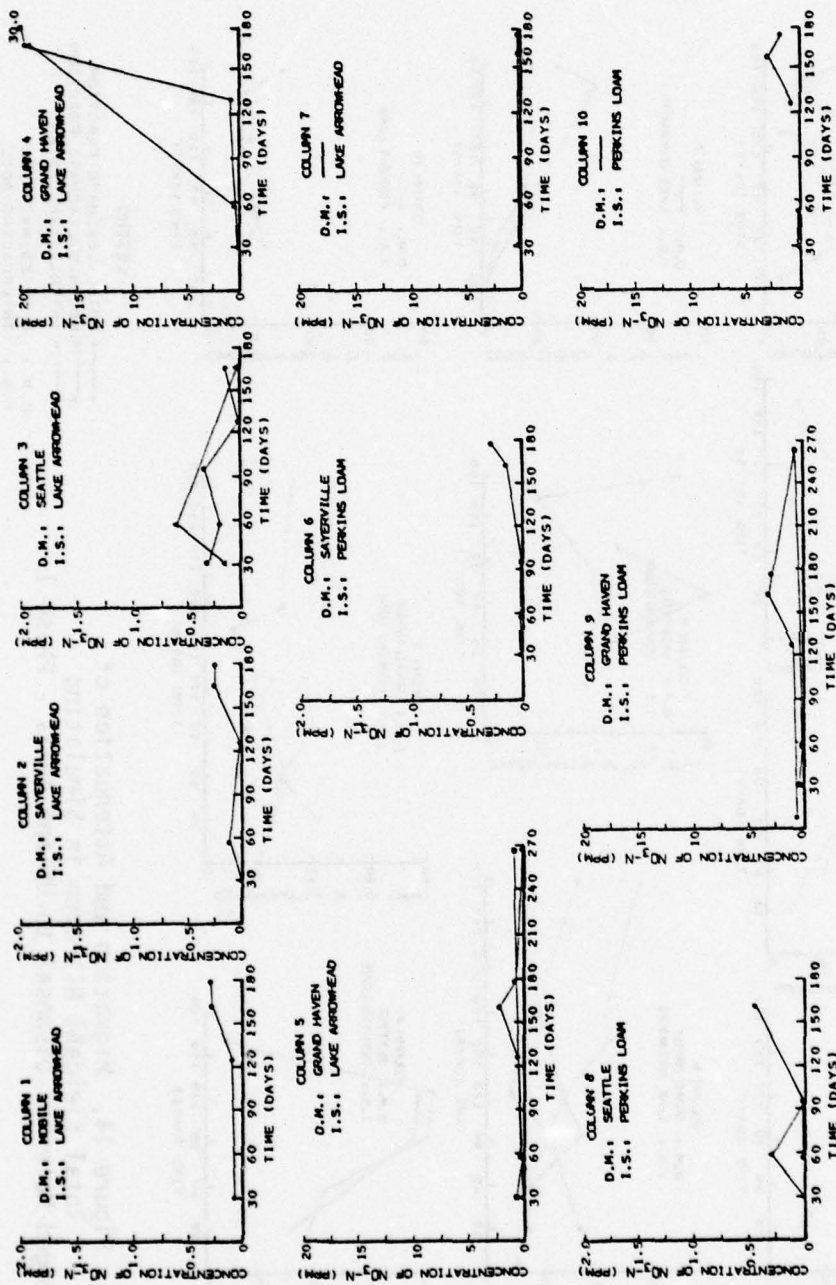


Figure 14. Migration and Attenuation of Total Kjeldahl Nitrogen in Simulating Dredged Material Disposal to Upland Areas - Phase I



LEGEND

- TOTAL LEACHATE FRACTION
- SOLUBLE LEACHATE FRACTION
- INTERSTITIAL WATER
- D.M.: DREDGED MATERIAL
- I.S.: INTERFACING SOIL

Figure 15. Migration and Attenuation of Nitrate-Nitrogen in Simulating Dredged Material Disposal to Upland Areas - Phase I

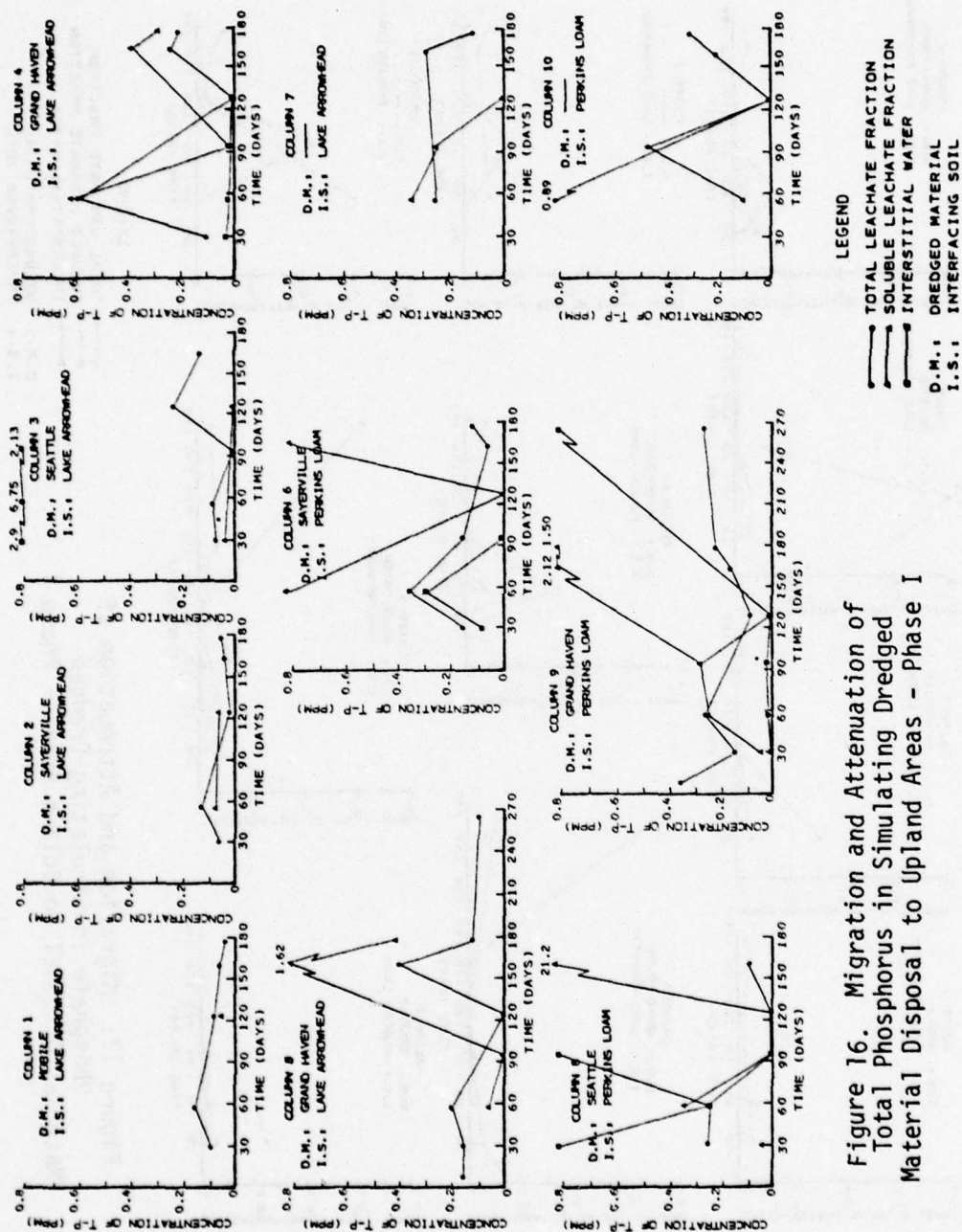


Figure 16. Migration and Attenuation of Total Phosphorus in Simulating Dredged Material Disposal to Upland Areas - Phase I

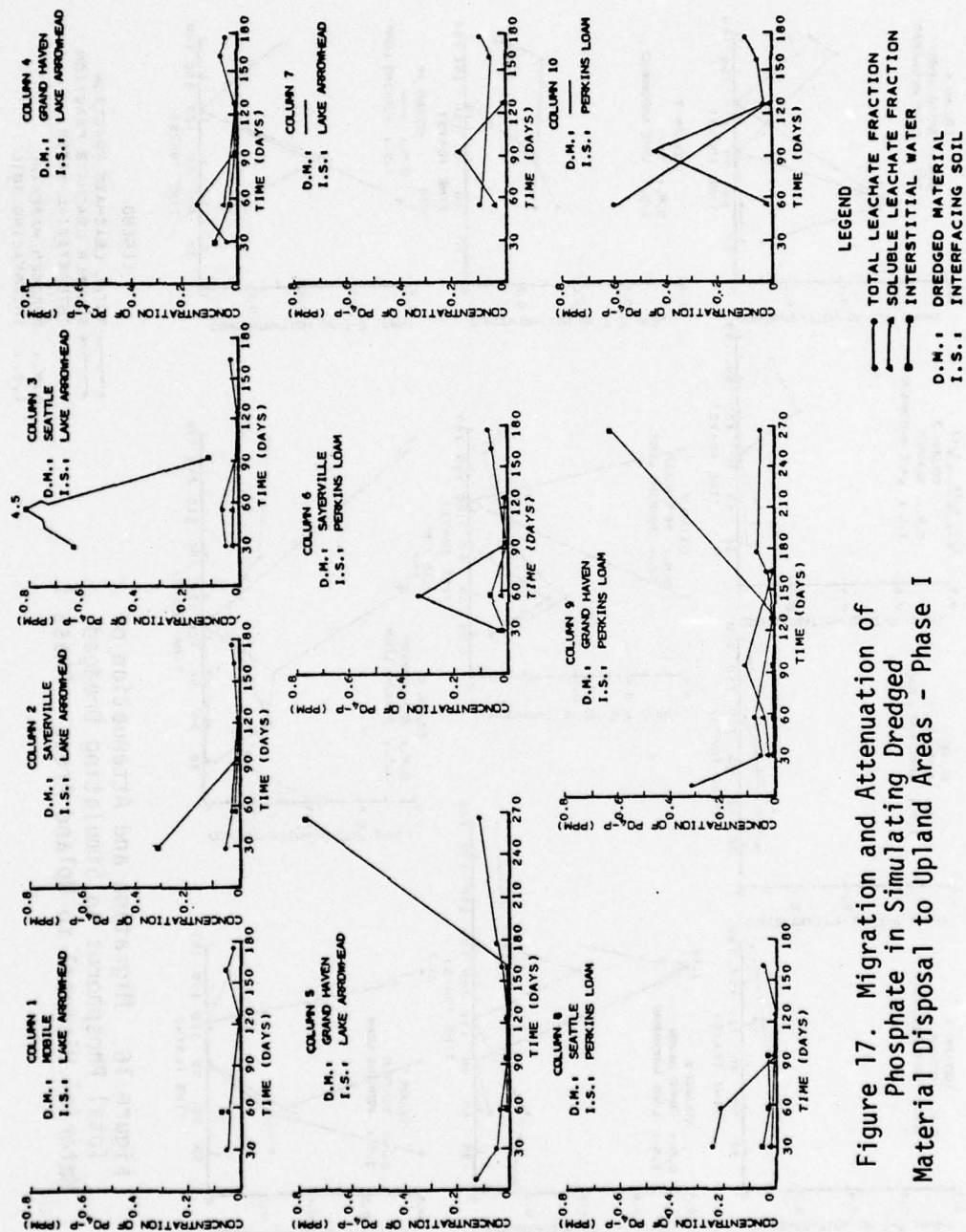


Figure 17. Migration and Attenuation of Phosphate in Simulating Dredged Material Disposal to Upland Areas - Phase I

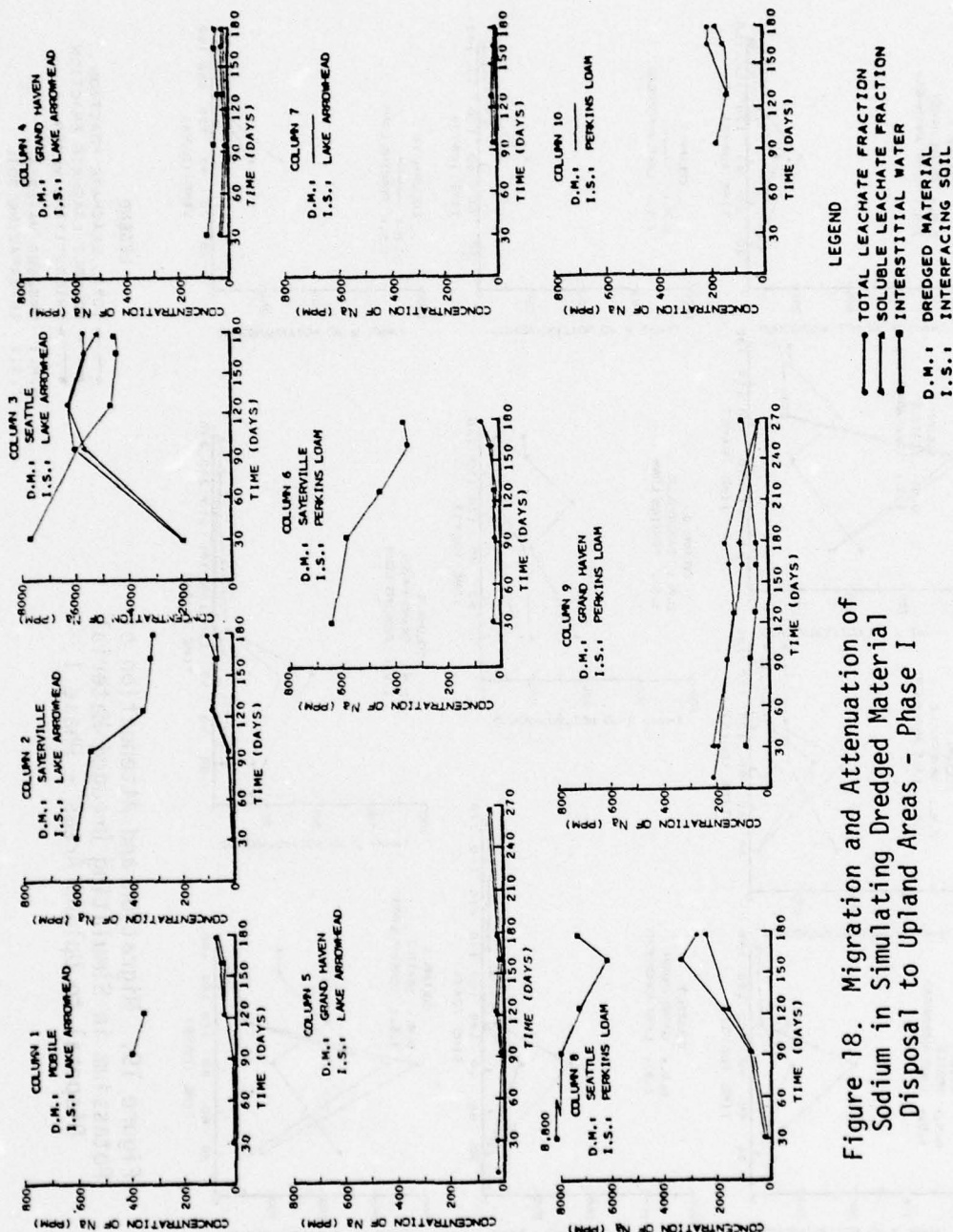


Figure 18. Migration and Attenuation of Sodium in Simulating Dredged Material Disposal to Upland Areas - Phase I

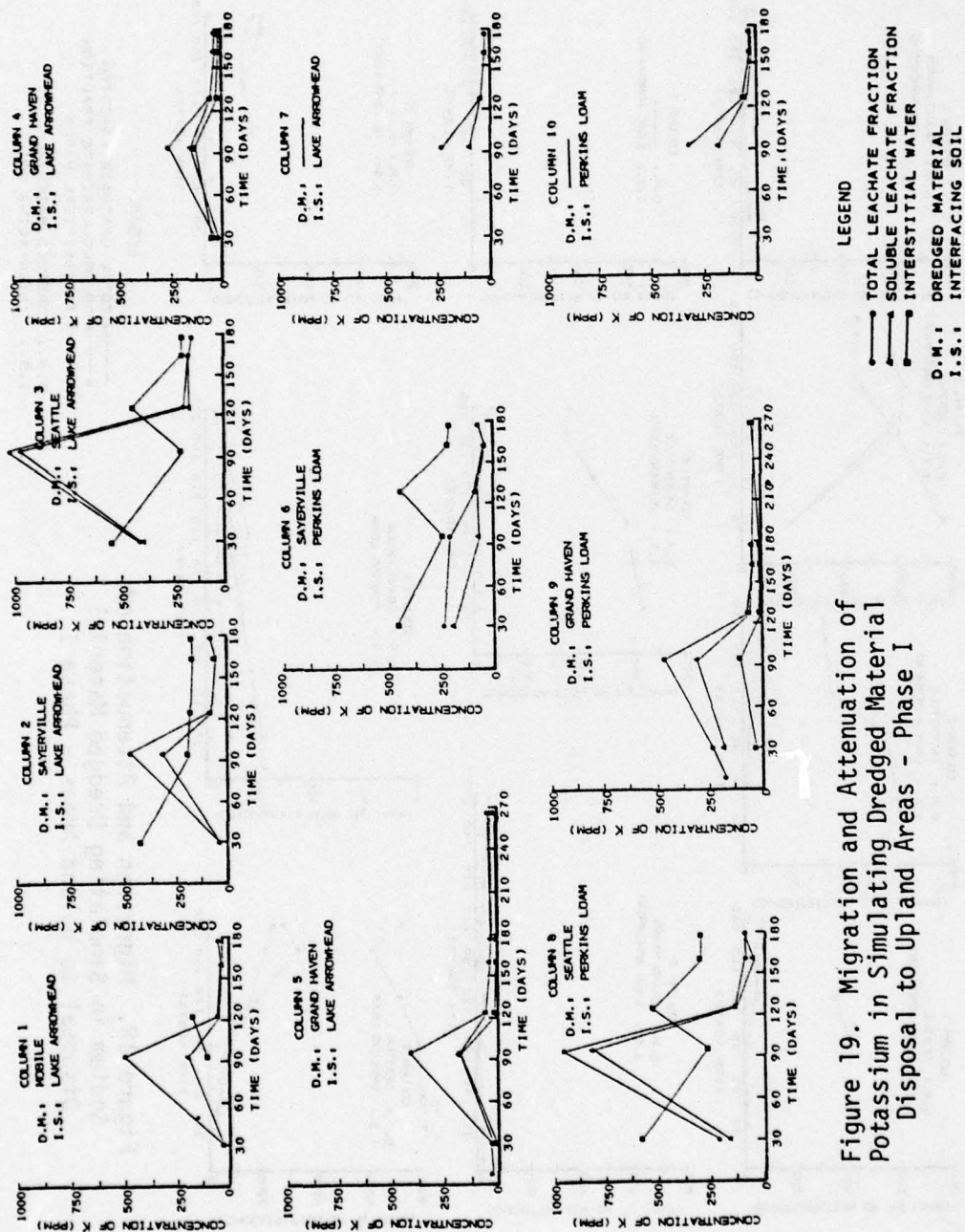


Figure 19. Migration and Attenuation of Potassium in Simulating Dredged Material Disposal to Upland Areas - Phase I

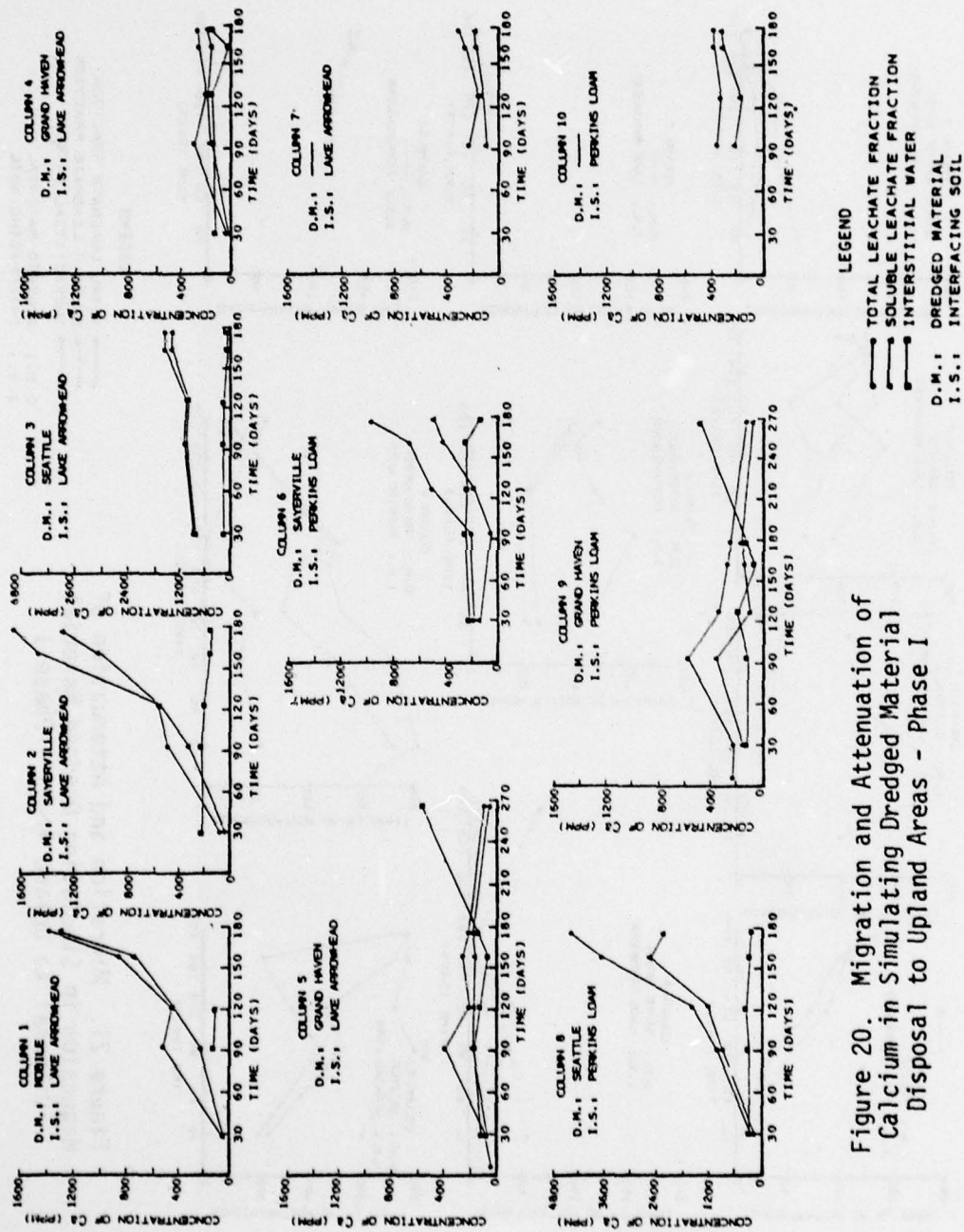


Figure 20. Migration and Attenuation of Calcium in Simulating Dredged Material Disposal to Upland Areas - Phase I

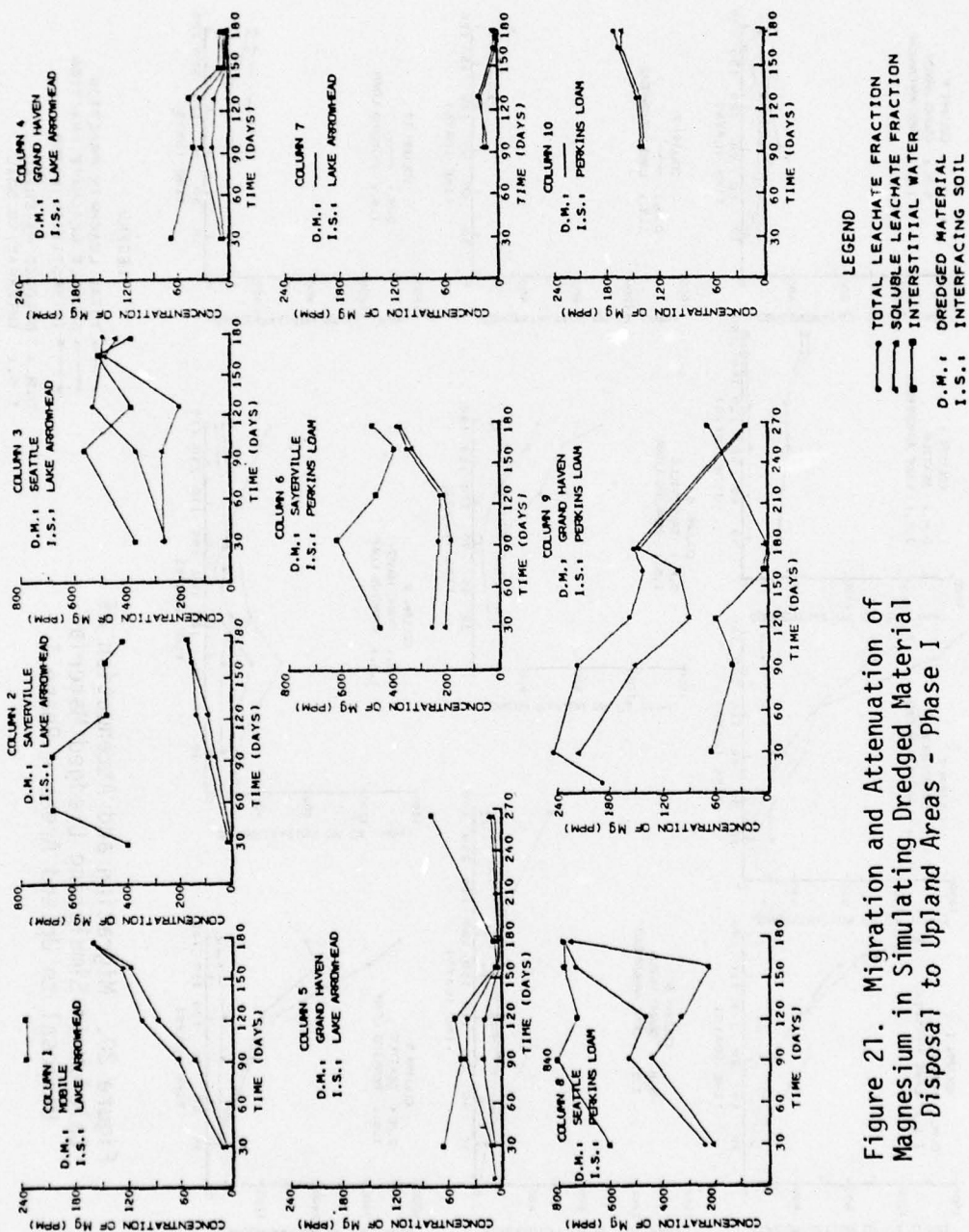


Figure 21. Migration and Attenuation of Magnesium in Simulating Dredged Material Disposal to Upland Areas - Phase I

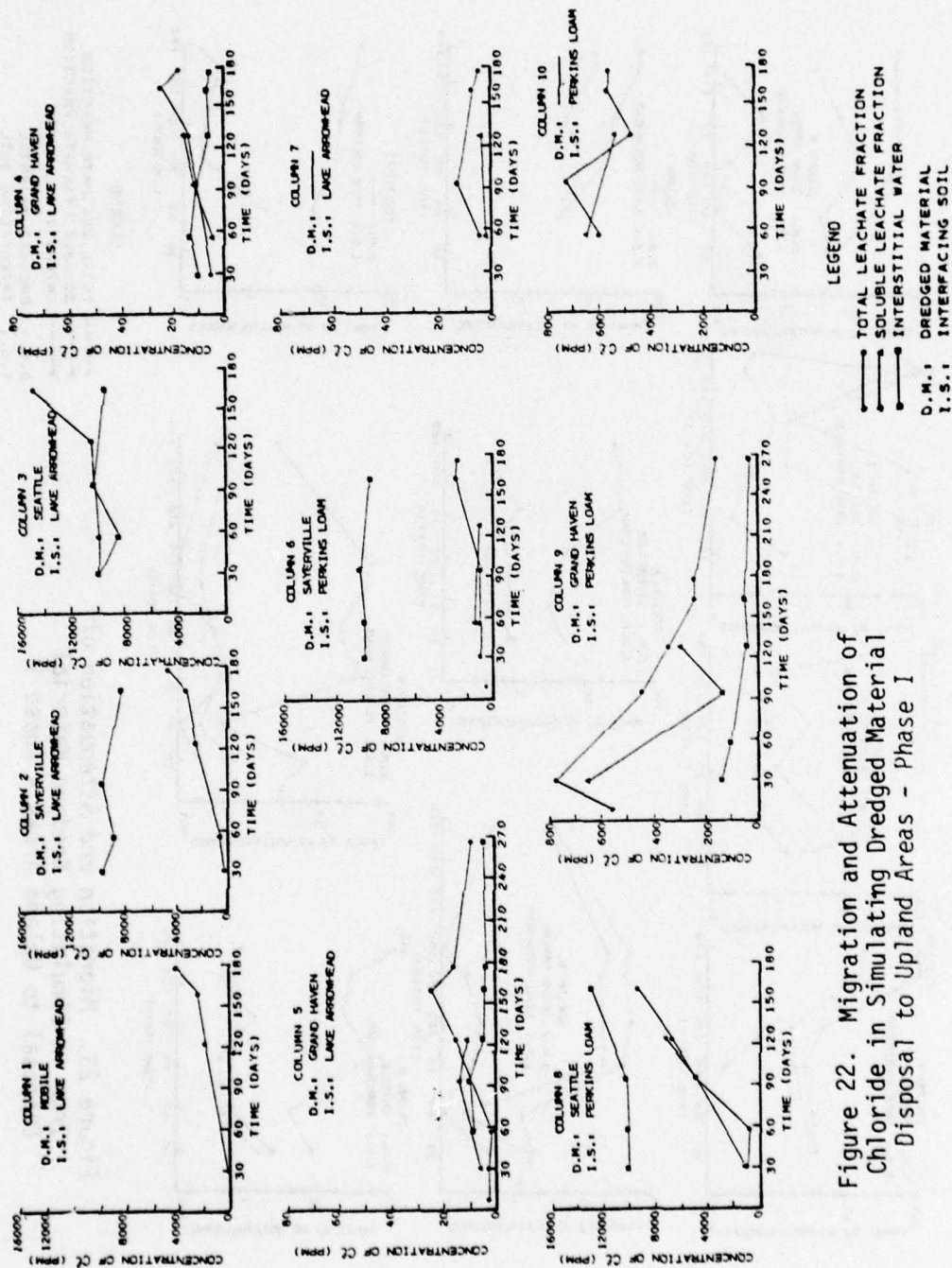
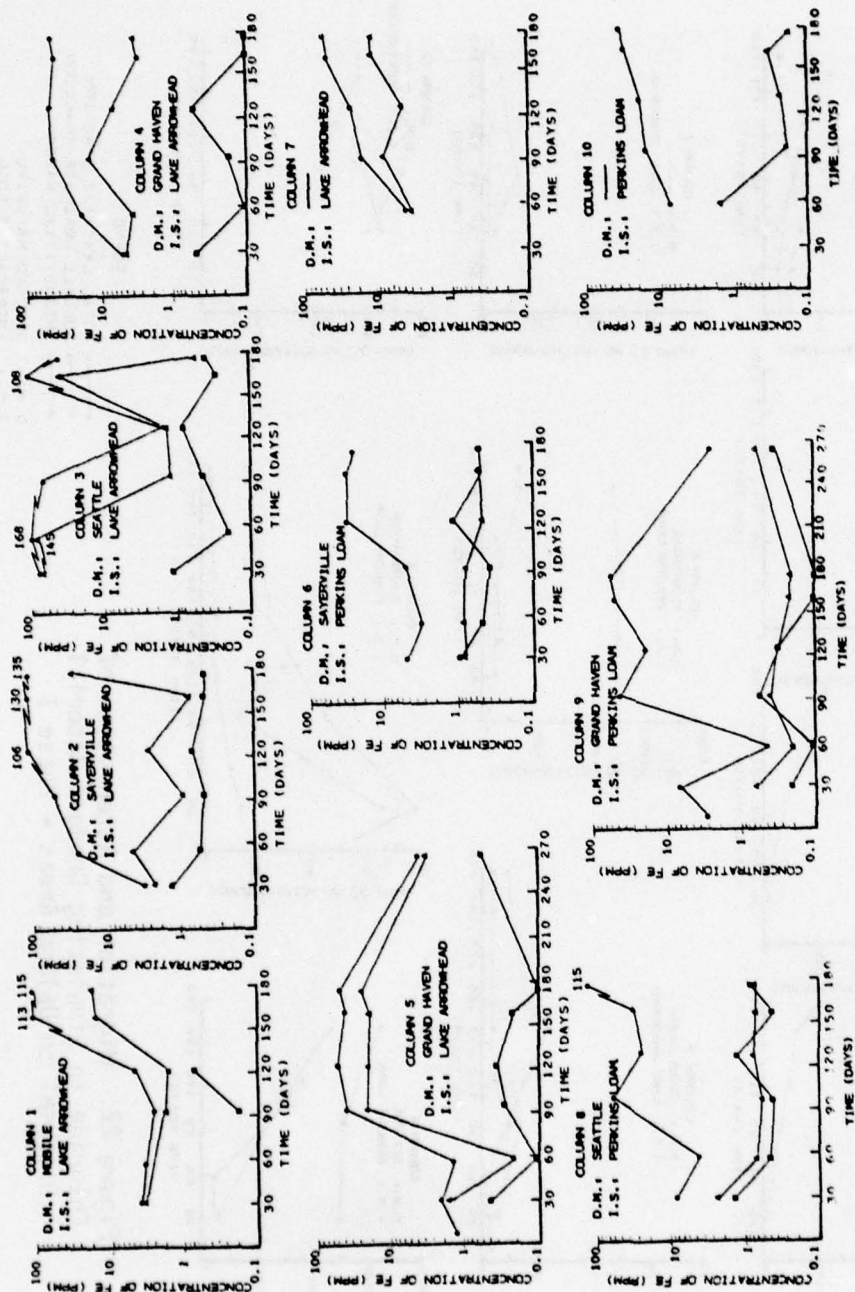


Figure 22. Migration and Attenuation of Chloride in Simulating Dredged Material Disposal to Upland Areas - Phase I



LEGEND

- TOTAL LEACHATE FRACTION
- SOLUBLE LEACHATE FRACTION
- △— INTERSTITIAL WATER
- ◇— DREDGED MATERIAL
- I.S.: DREDGED MATERIAL
- I.S.: INTERFACING SOIL

Figure 23. Migration and Attenuation of Iron in Simulating Dredged Material Disposal to Upland Areas - Phase I

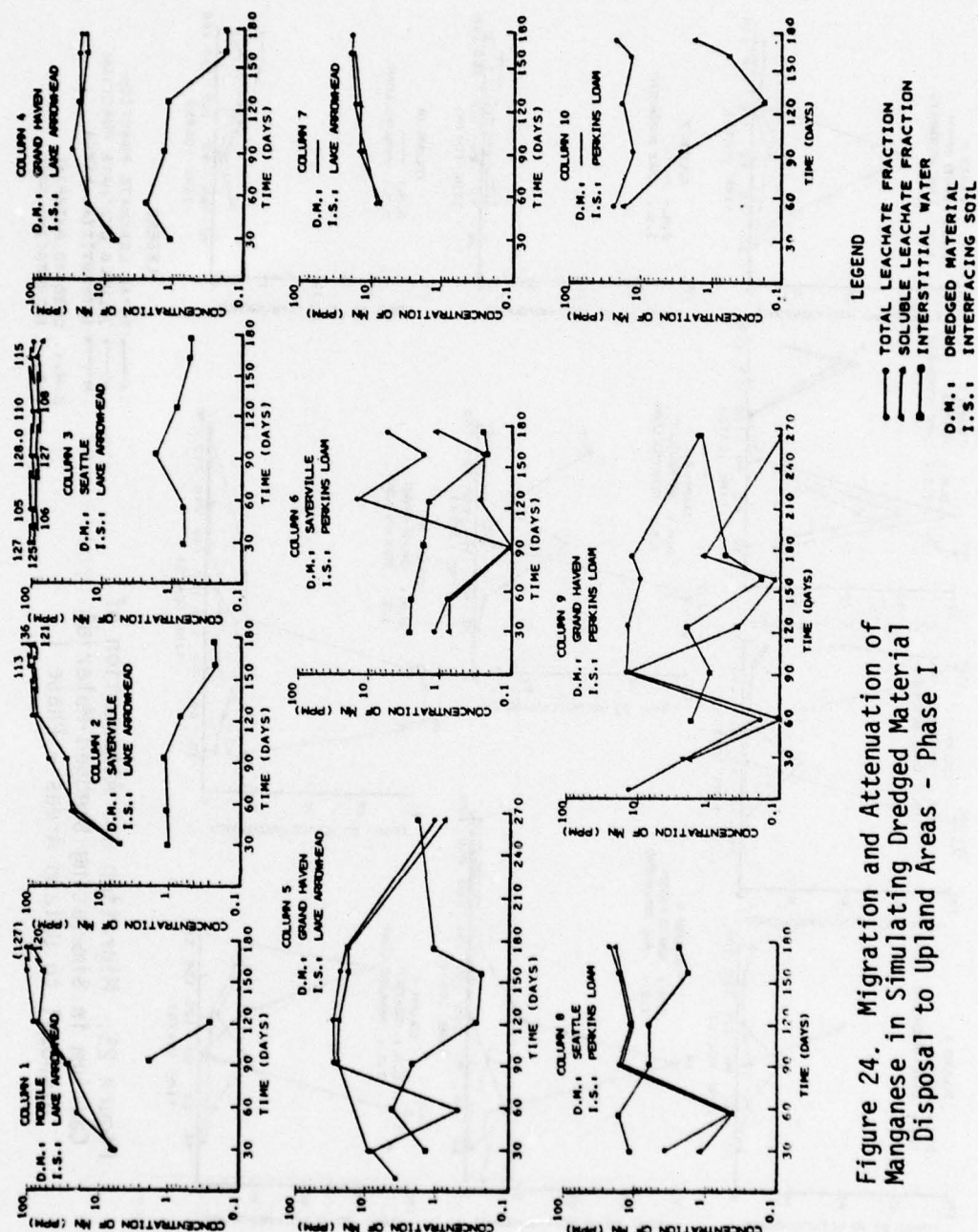


Figure 24. Migration and Attenuation of Manganese in Simulating Dredged Material Disposal to Upland Areas - Phase I

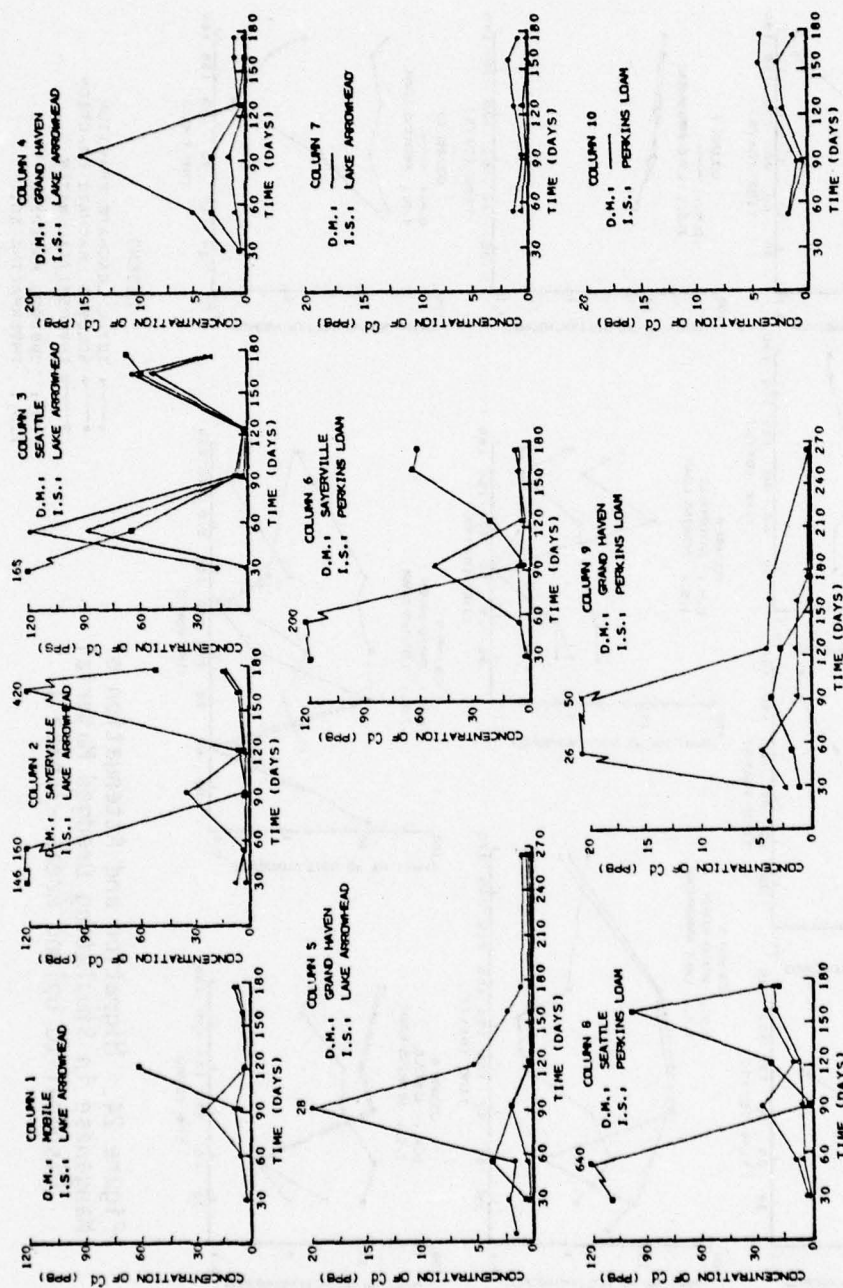


Figure 25. Migration and Attenuation of Cadmium in Simulating Dredged Material Disposal to Upland Areas - Phase I

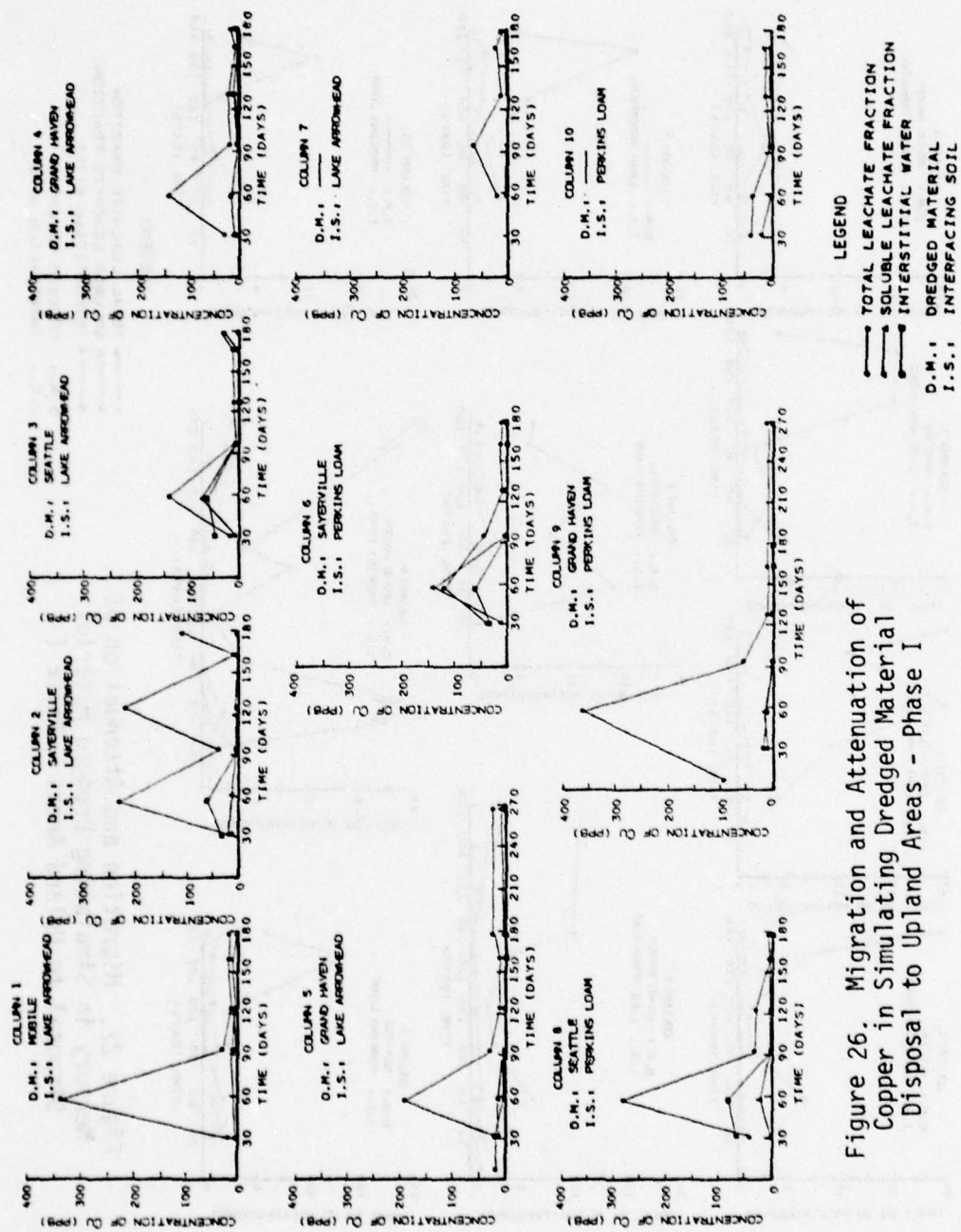


Figure 26. Migration and Attenuation of Copper in Simulating Dredged Material Disposal to Upland Areas - Phase I

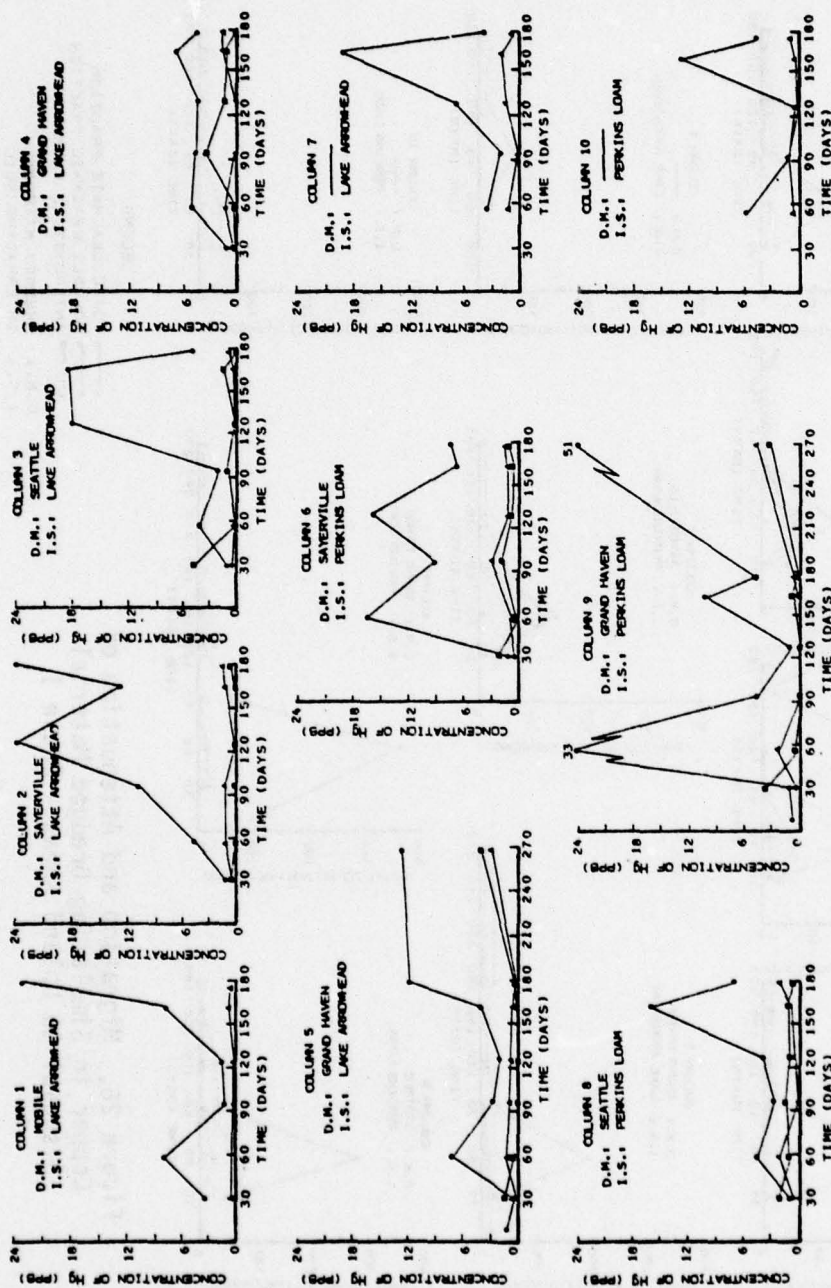


Figure 27. Migration and Attenuation of Mercury in Simulating Dredged Material Disposal to Upland Areas - Phase I

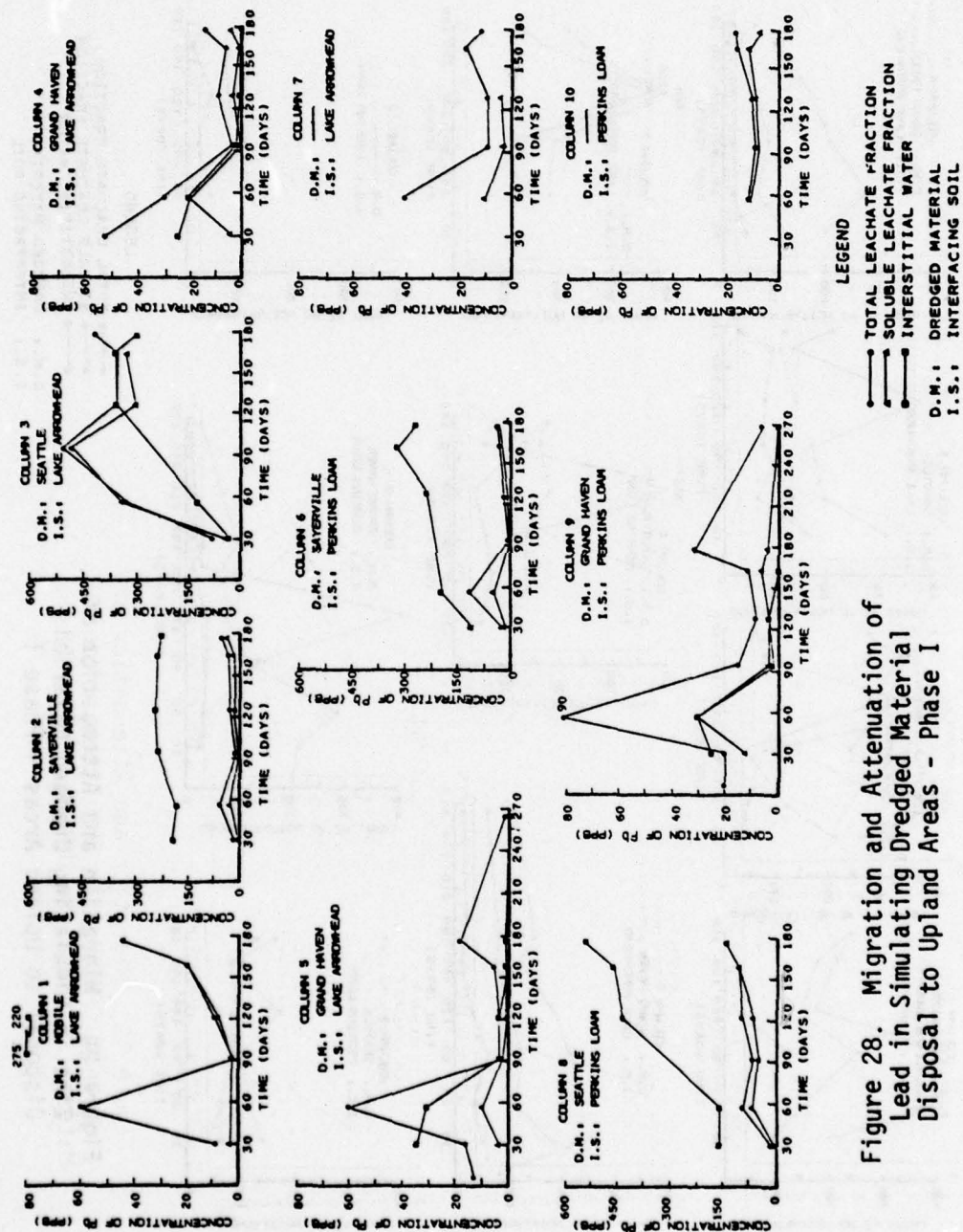


Figure 28. Migration and Attenuation of Lead in Simulating Dredged Material Disposal to Upland Areas - Phase I

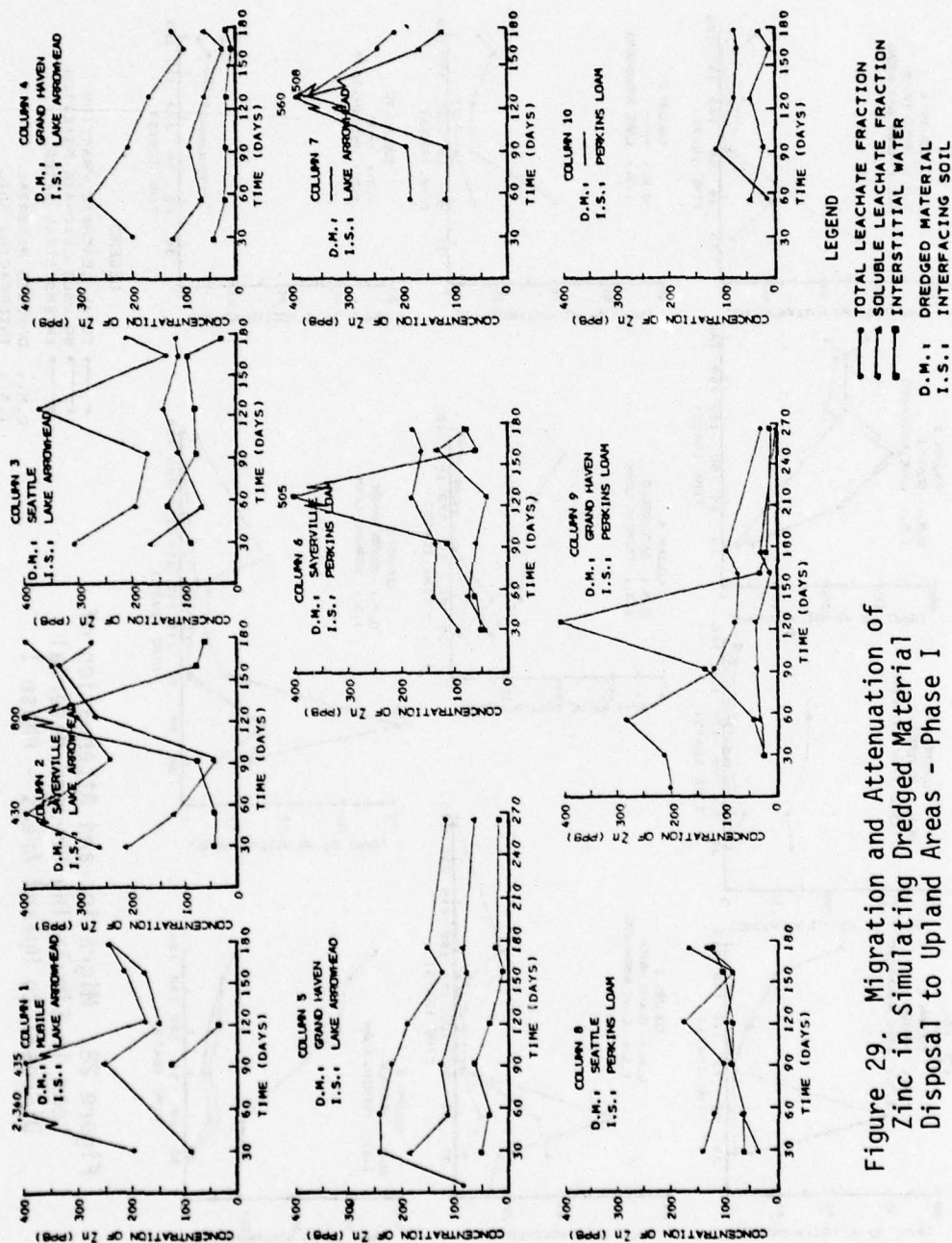


Figure 29. Migration and Attenuation of Zinc in Simulating Dredged Material Disposal to Upland Areas - Phase I

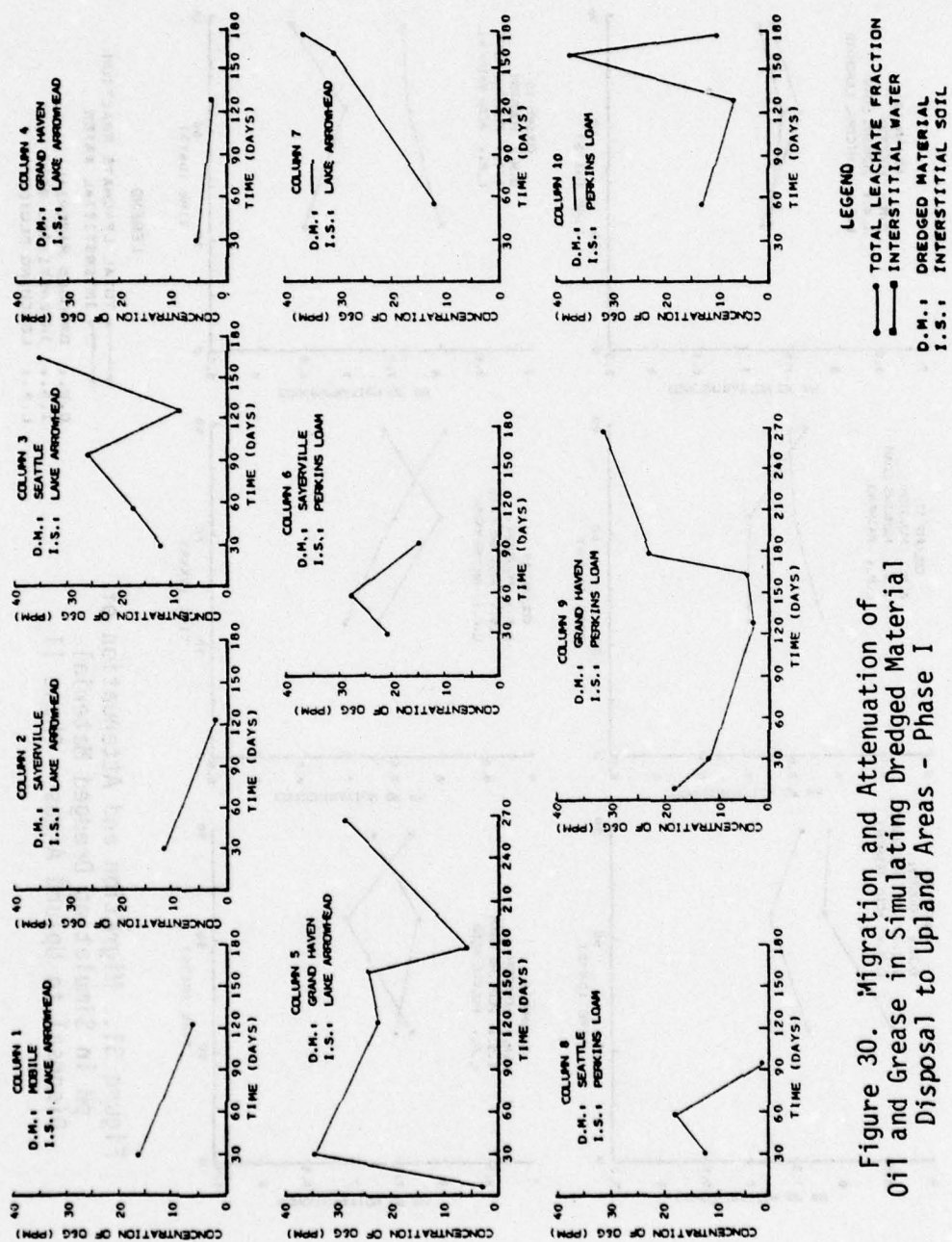
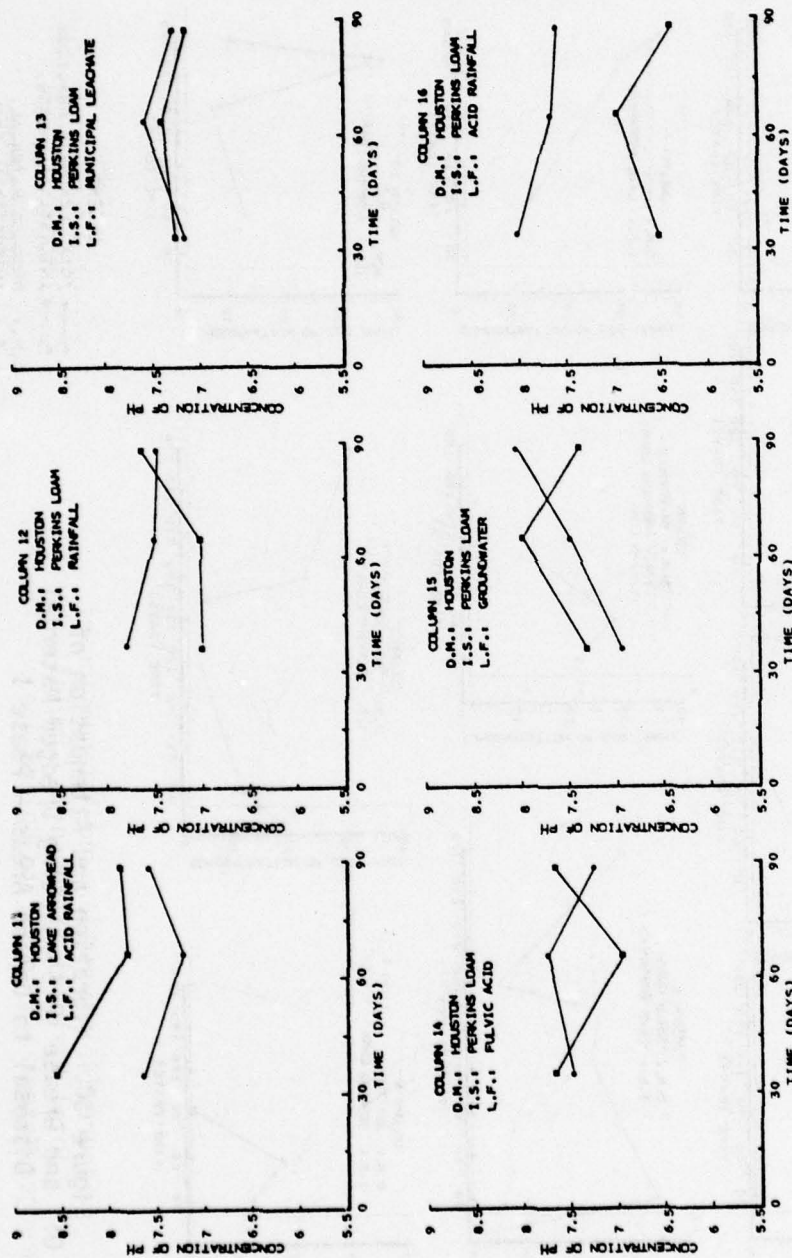


Figure 30. Migration and Attenuation of Oil and Grease in Simulating Dredged Material Disposal to Upland Areas - Phase I



LEGEND

— TOTAL LEACHATE FRACTION
— INTERSTITIAL WATER
— D.M.: DREDGED MATERIAL
— I.S.: INTERSTITIAL SOIL
— L.P.: LEACHING FLUID

Figure 31. Migration and Attenuation of pH in Simulating Dredged Material Disposal to Upland Areas - Phase II

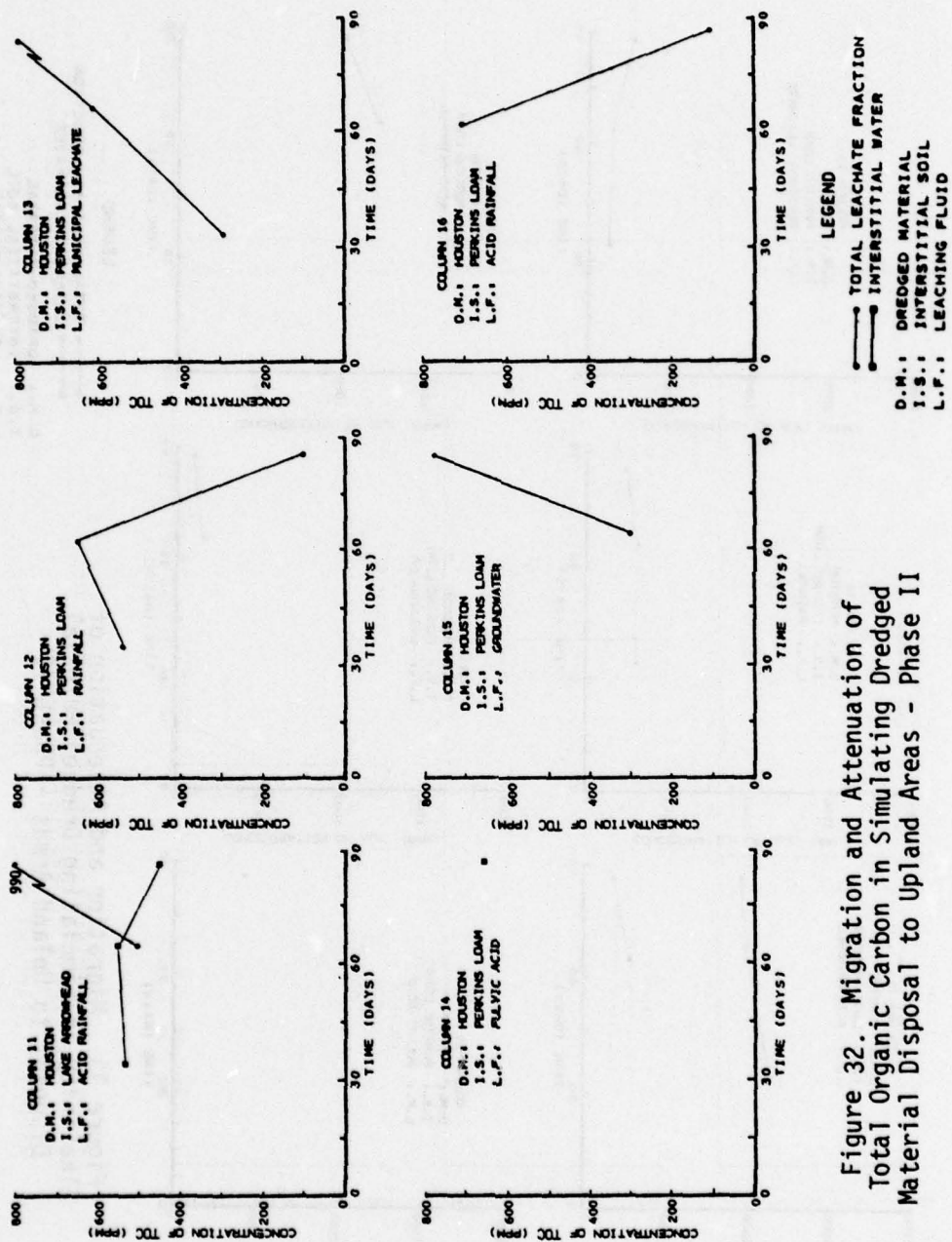


Figure 32. Migration and Attenuation of Total Organic Carbon in Simulating Dredged Material Disposal to Upland Areas - Phase II

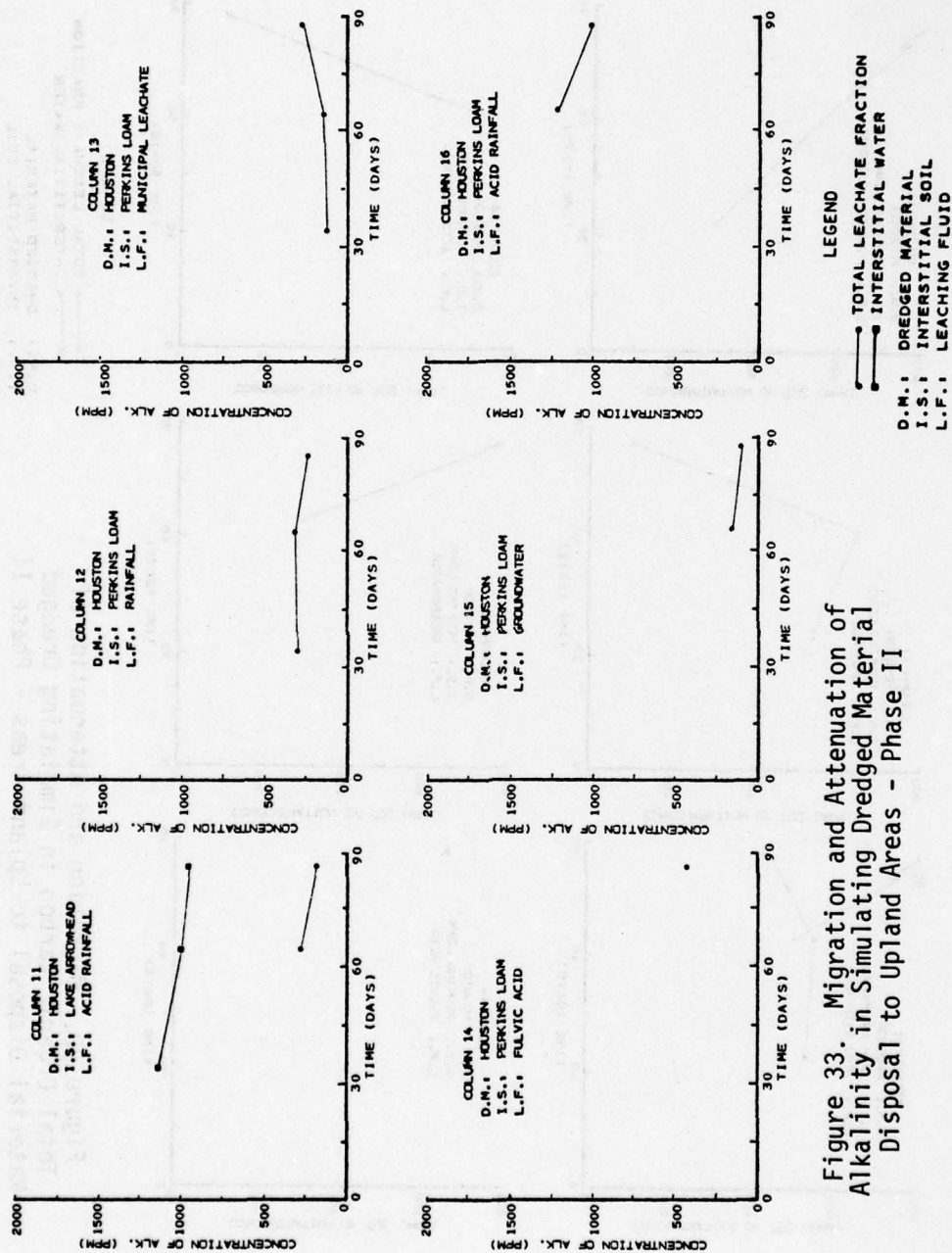
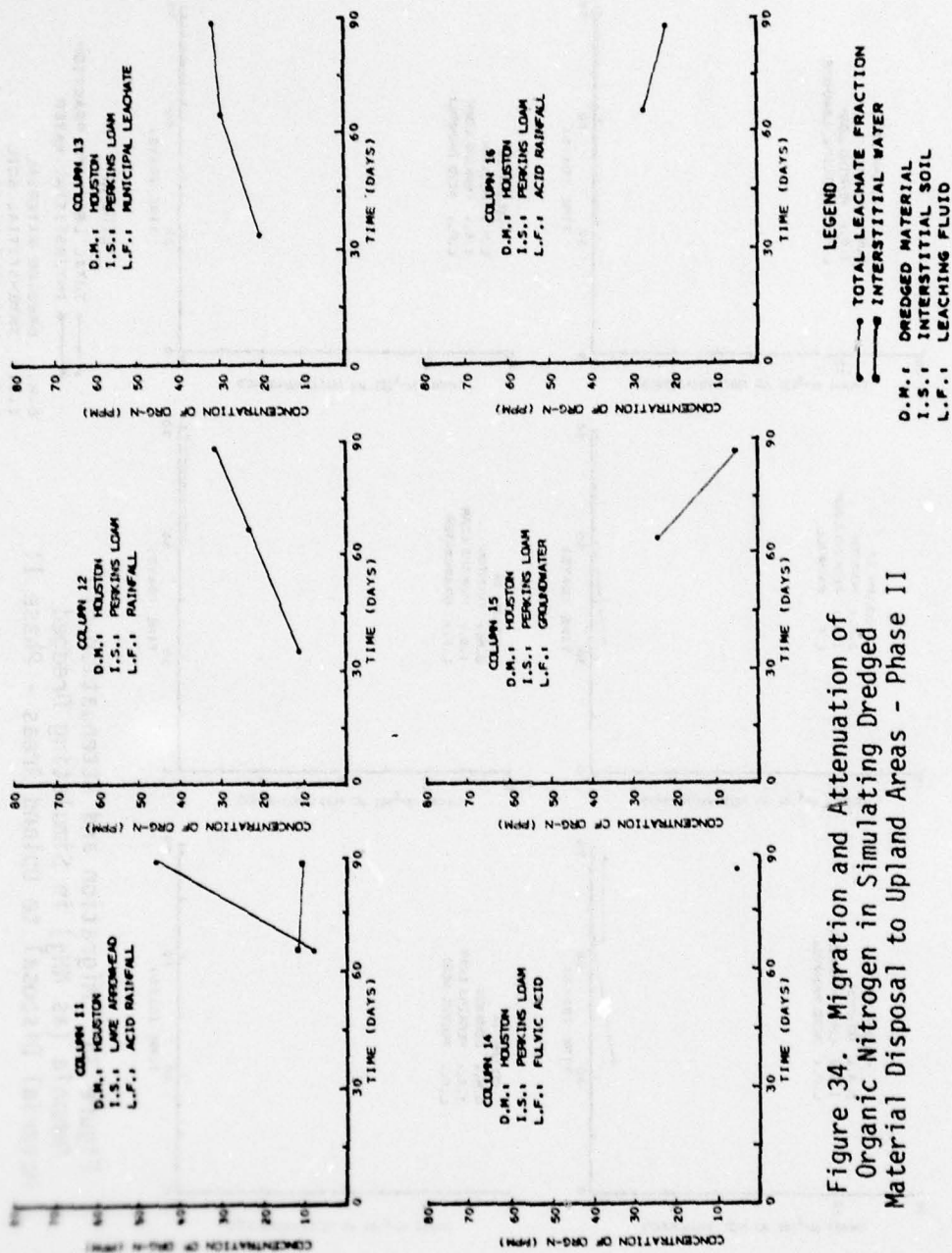


Figure 33. Migration and Attenuation of Alkalinity in Simulating Dredged Material Disposal to Upland Areas - Phase II



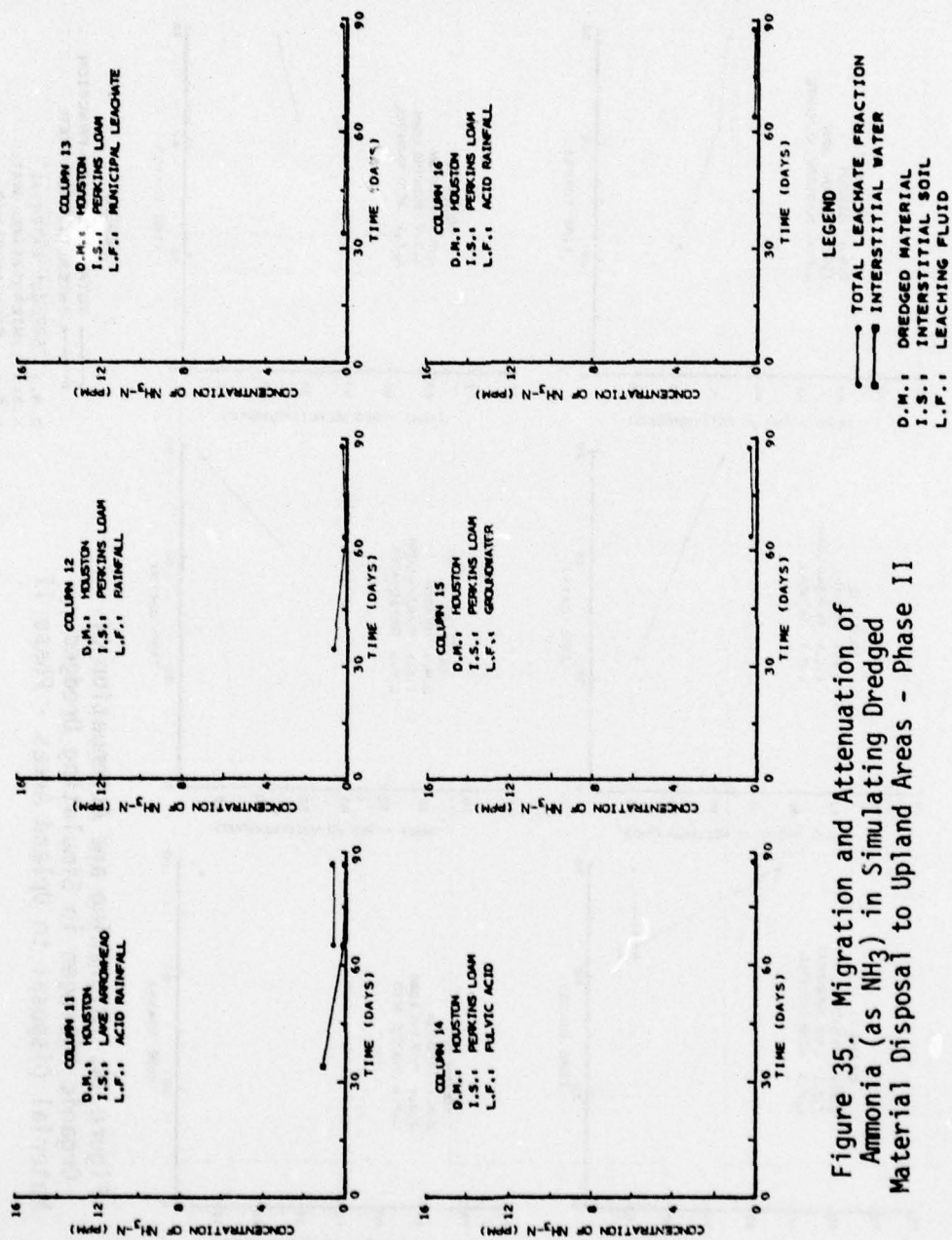


Figure 35. Migration and Attenuation of Ammonia (as NH_3) in Simulating Dredged Material Disposal to Upland Areas - Phase II

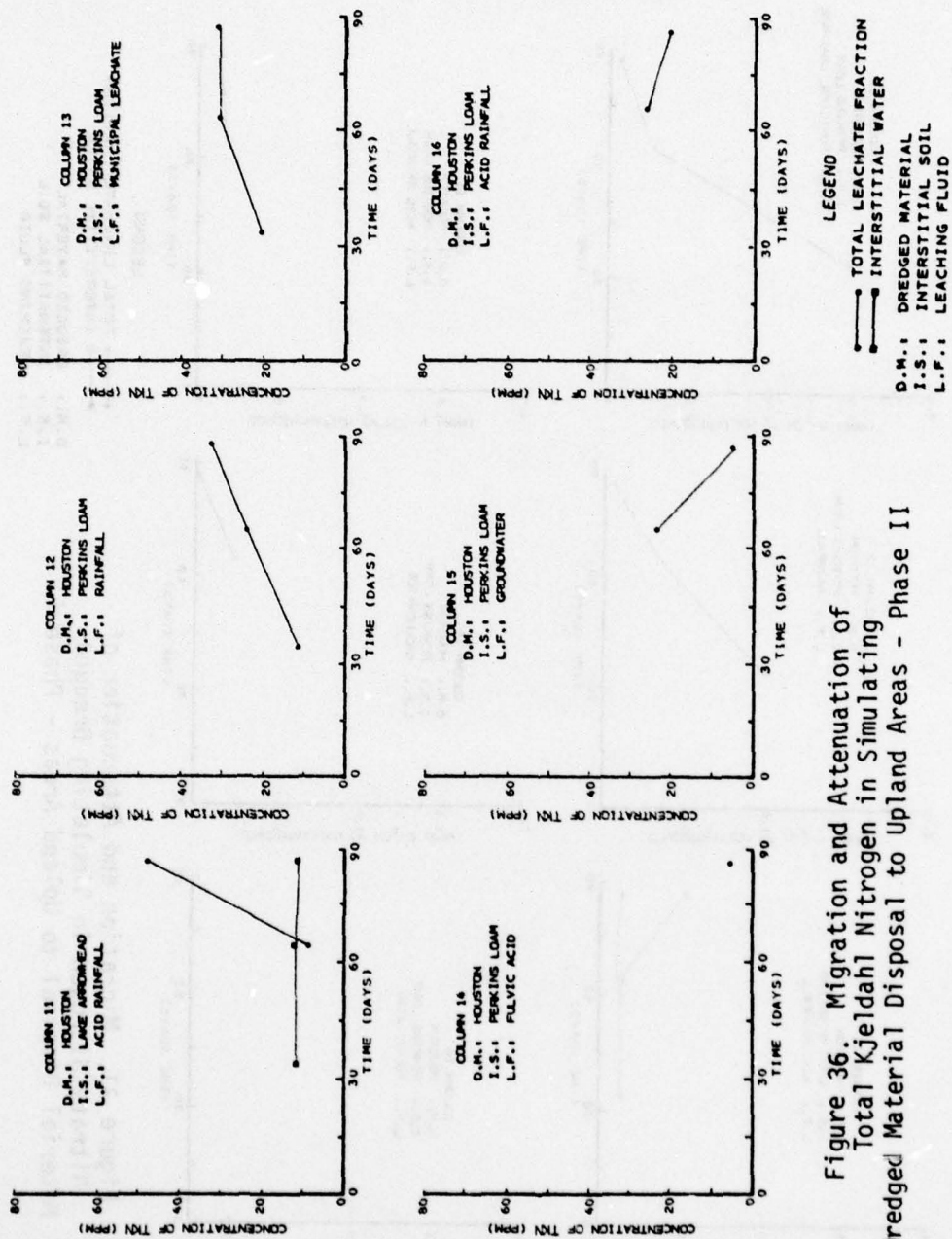


Figure 36. Migration and Attenuation of Total Kjeldahl Nitrogen in Simulating Dredged Material Disposal to Upland Areas - Phase II

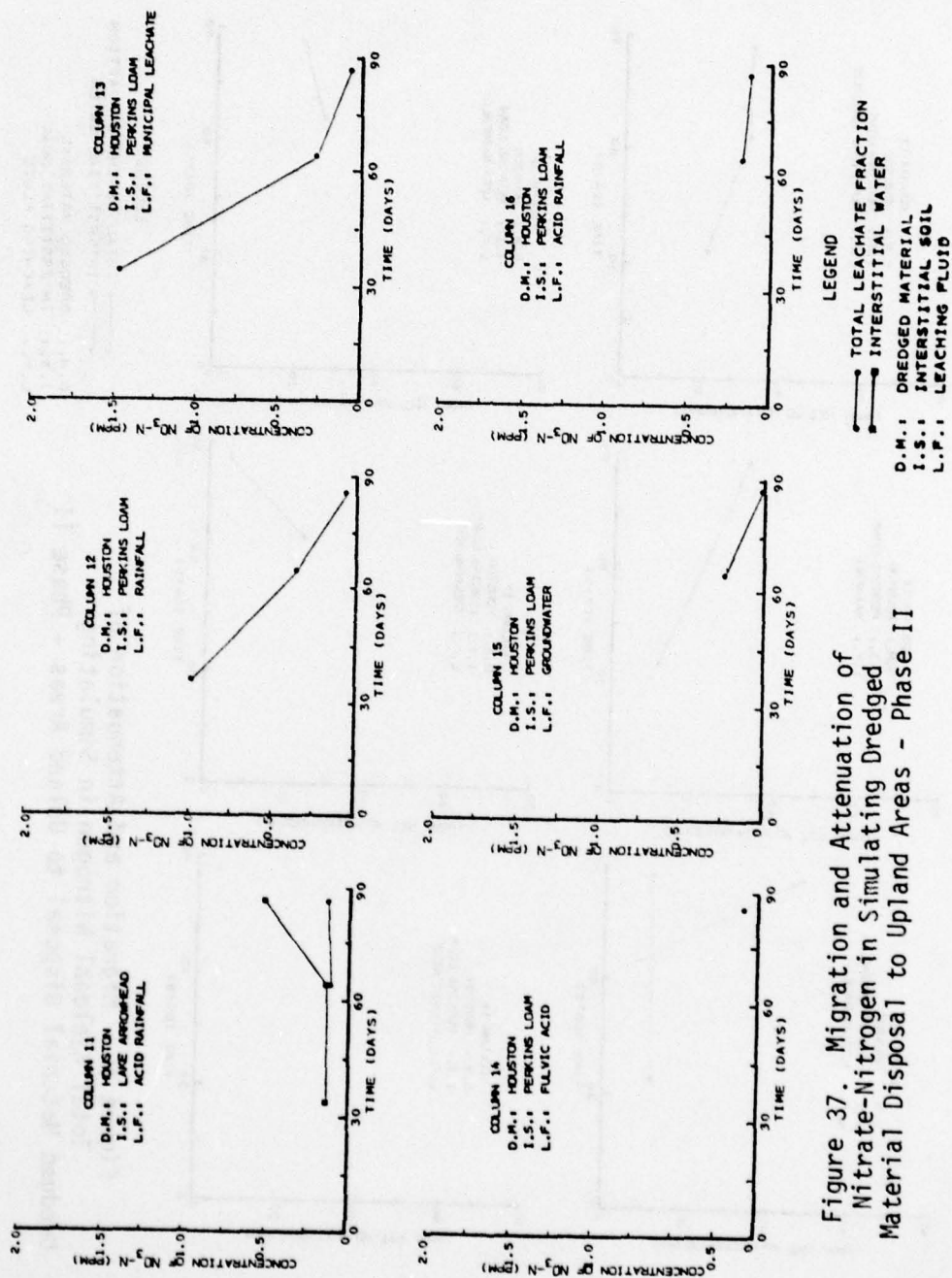


Figure 37. Migration and Attenuation of Nitrate-Nitrogen in Simulating Dredged Material Disposal to Upland Areas - Phase II

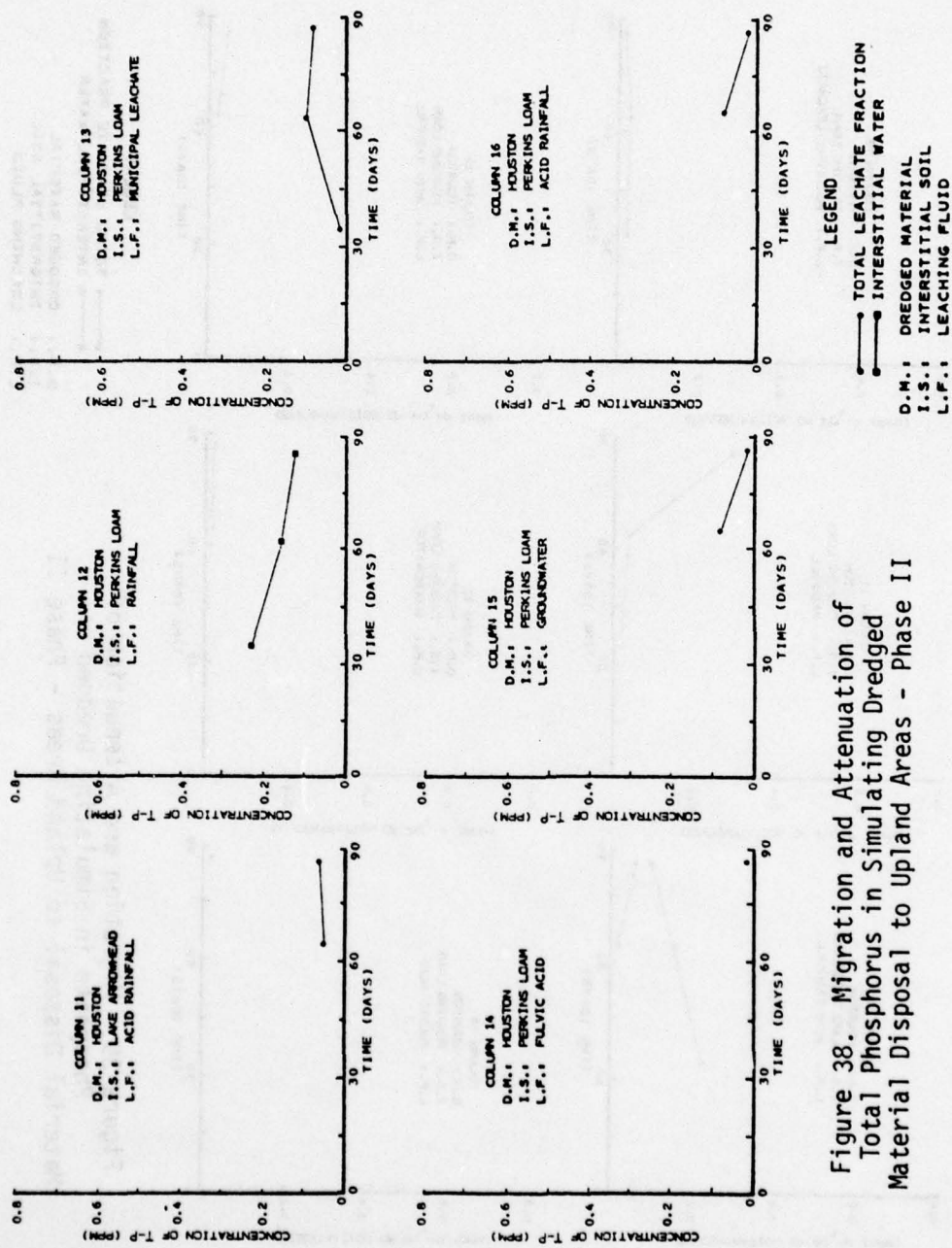


Figure 38. Migration and Attenuation of
Total Phosphorus in Simulating Dredged
Material Disposal to Upland Areas - Phase II

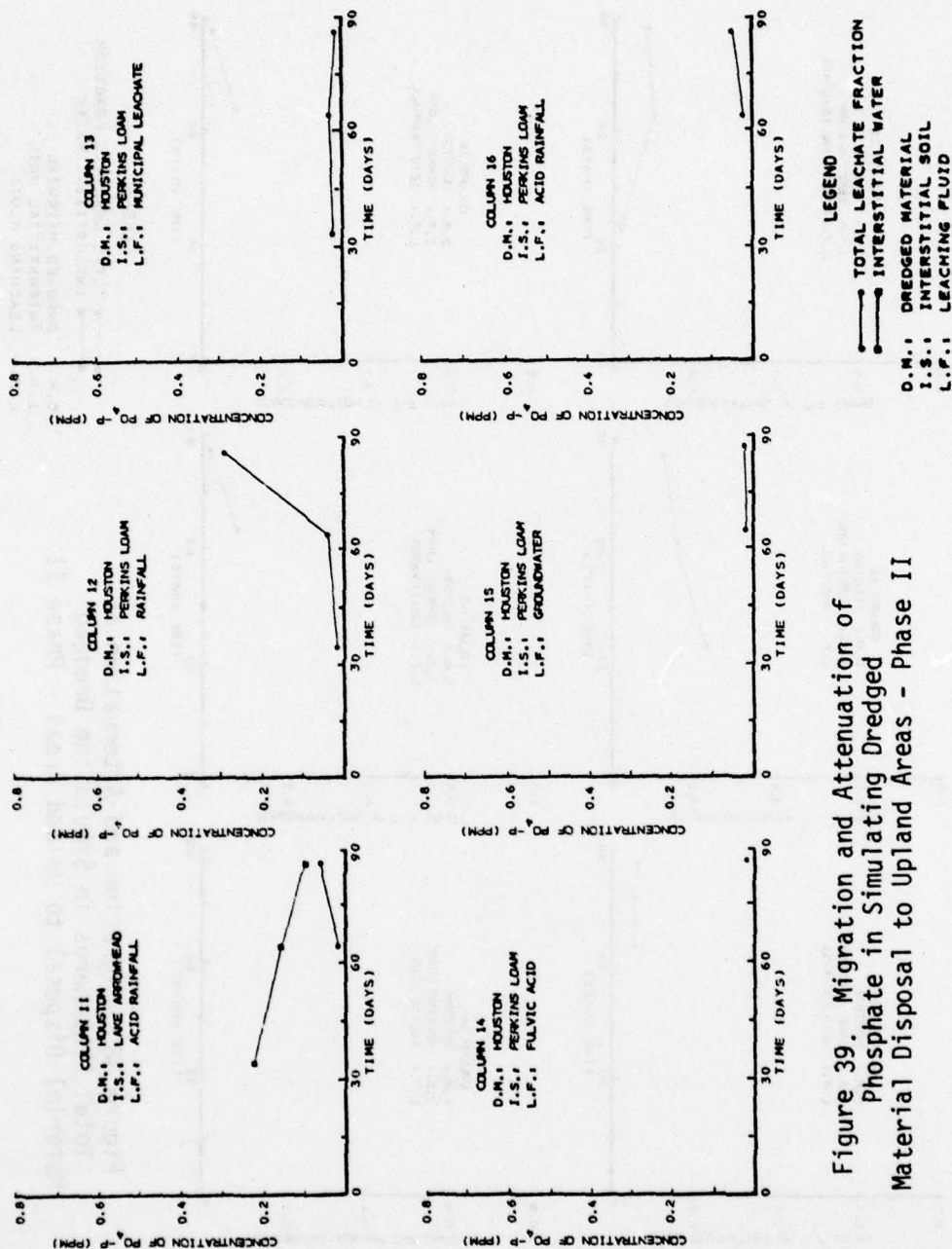
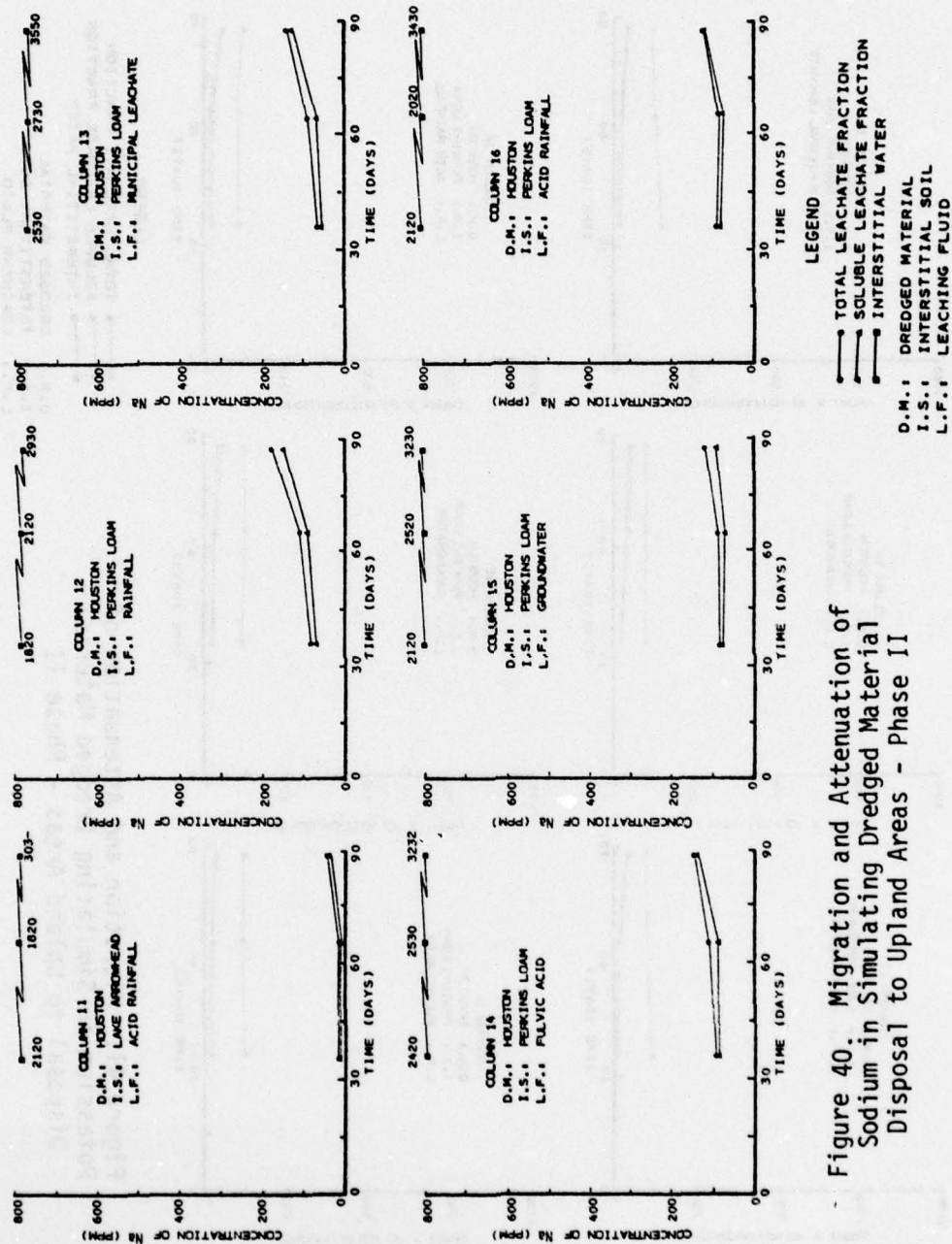


Figure 39. Migration and Attenuation of Phosphate in Simulating Dredged Material Disposal to Upland Areas - Phase II



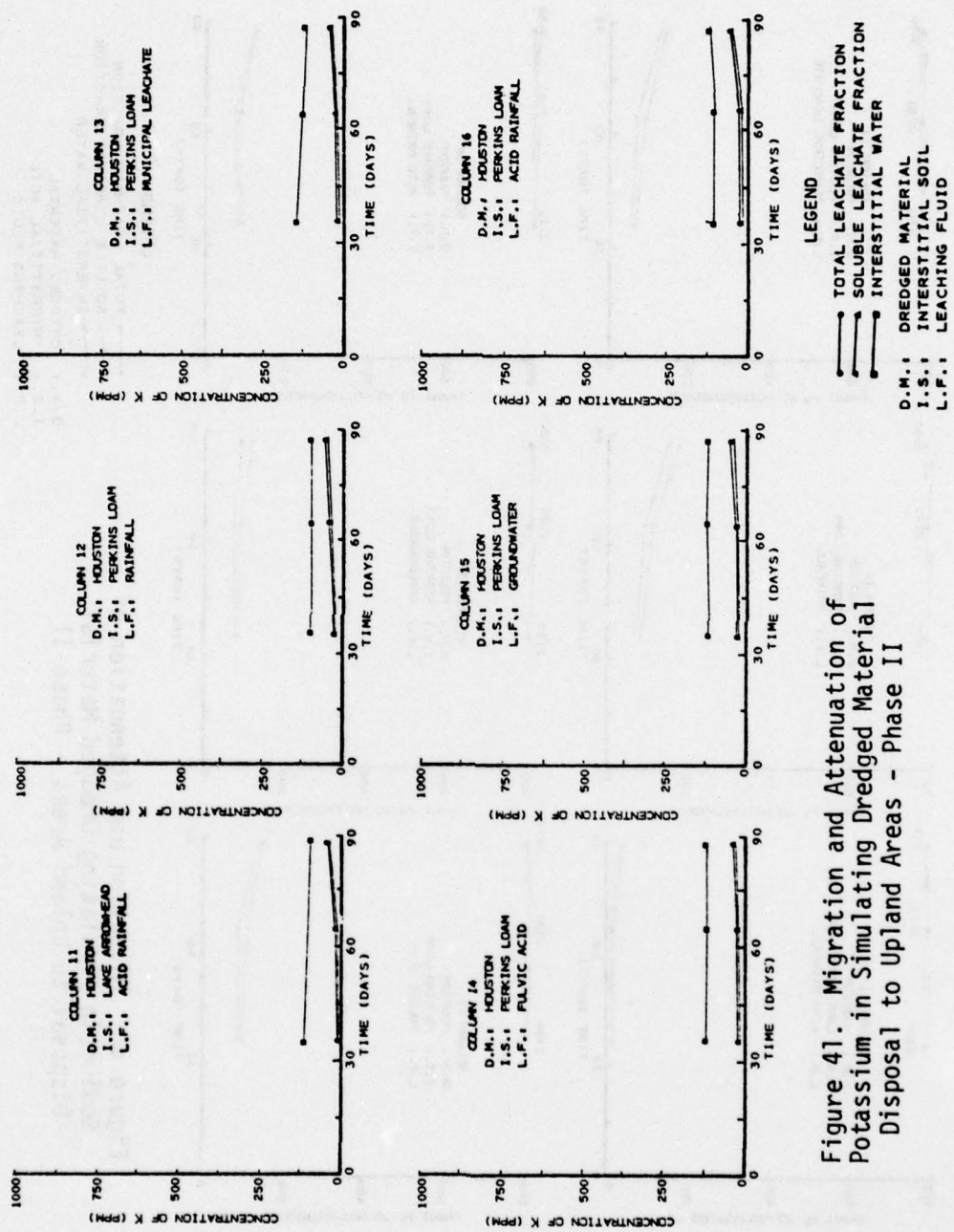
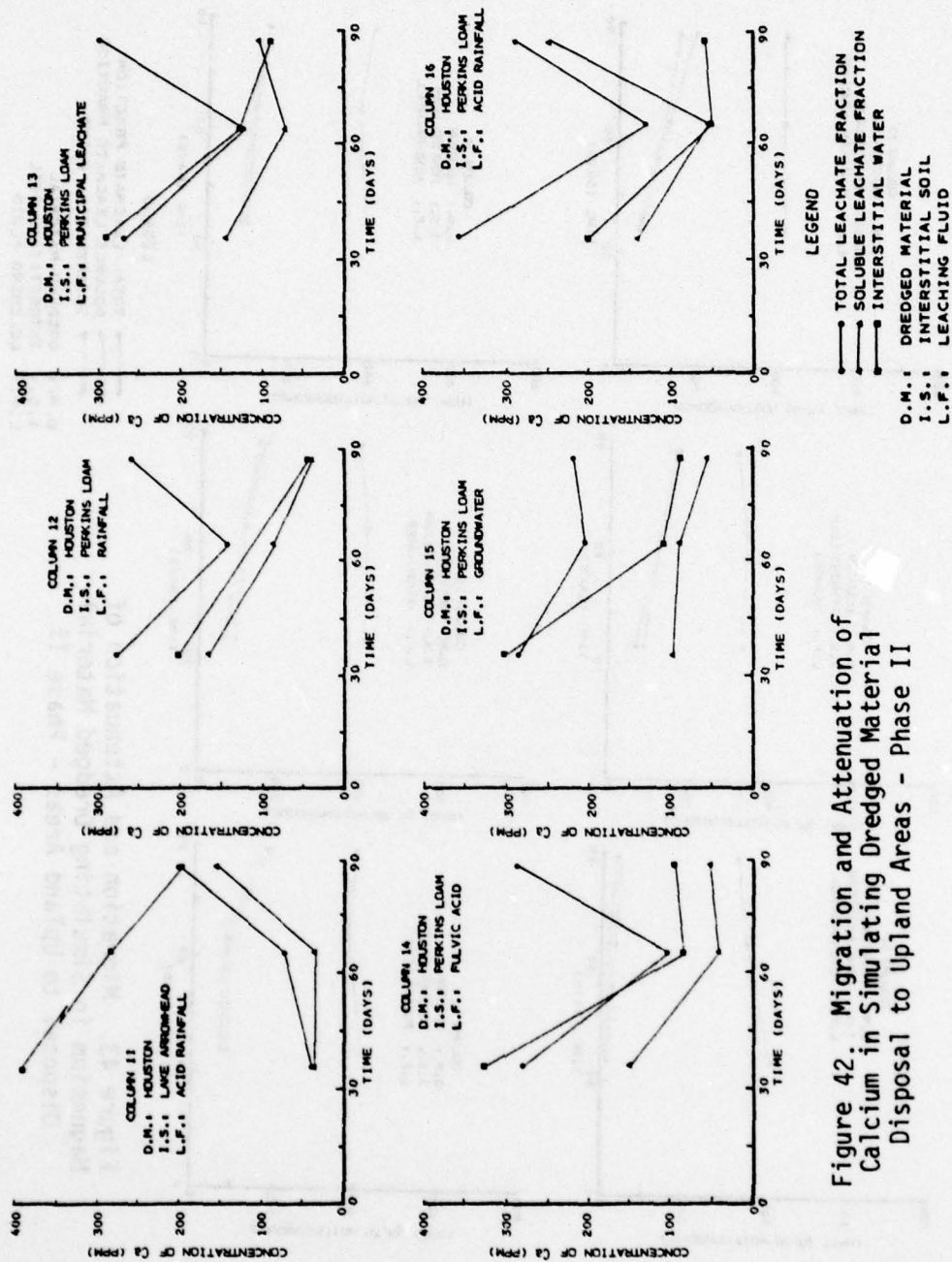


Figure 41. Migration and Attenuation of Potassium in Simulating Dredged Material Disposal to Upland Areas - Phase II



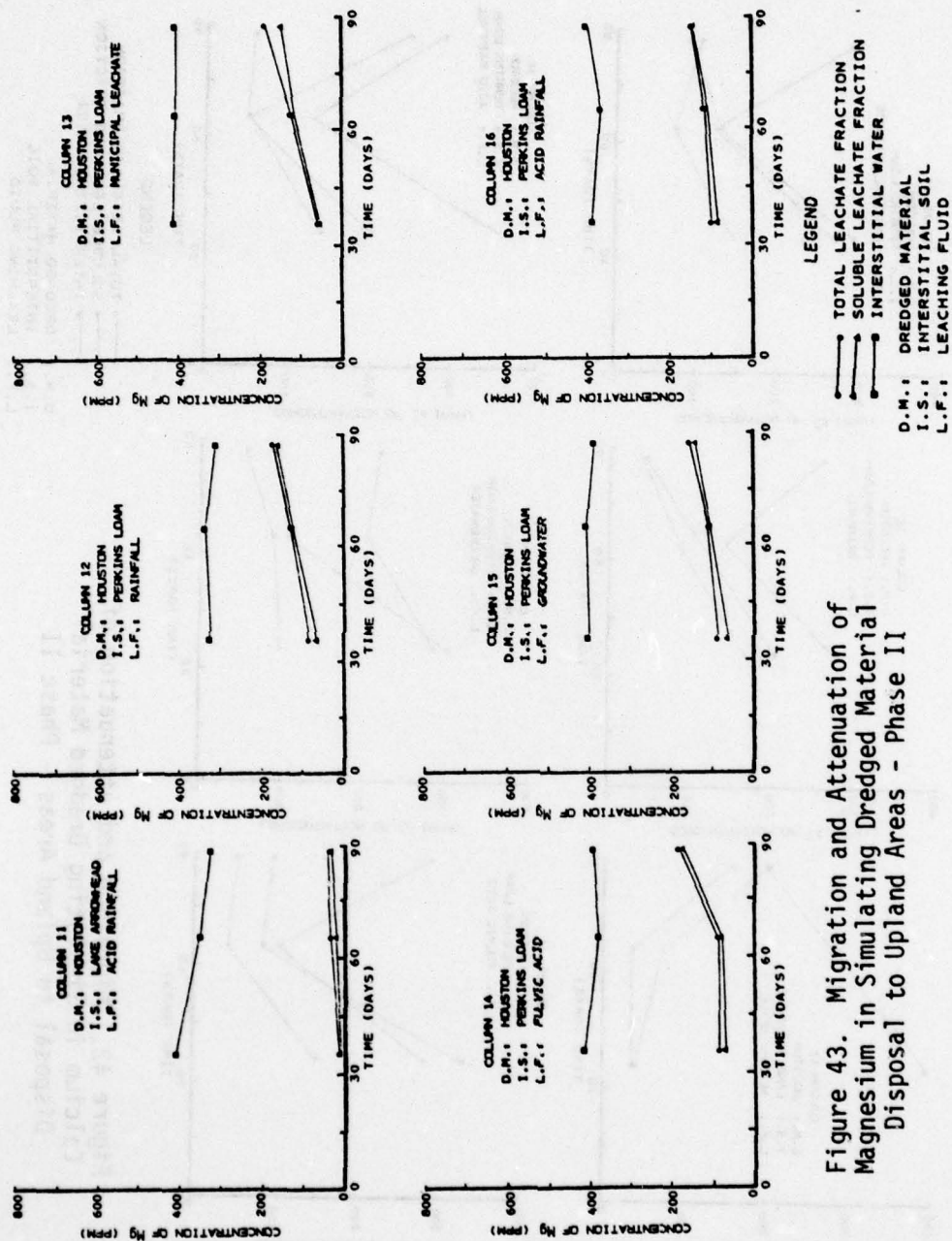


Figure 43. Migration and Attenuation of Magnesium in Simulating Dredged Material Disposal to Upland Areas - Phase II

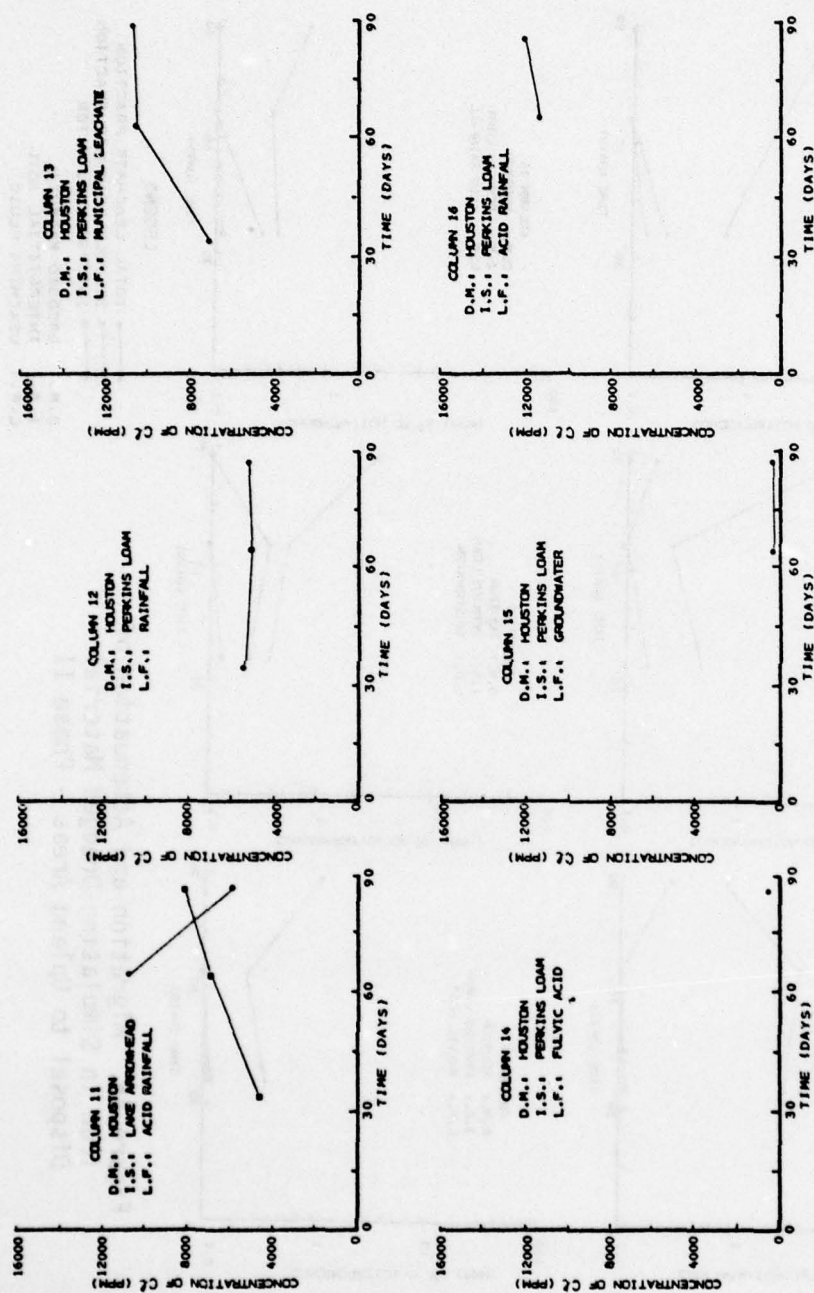


Figure 44. Migration and Attenuation of Chloride in Simulating Dredged Material Disposal to Upland Areas - Phase II

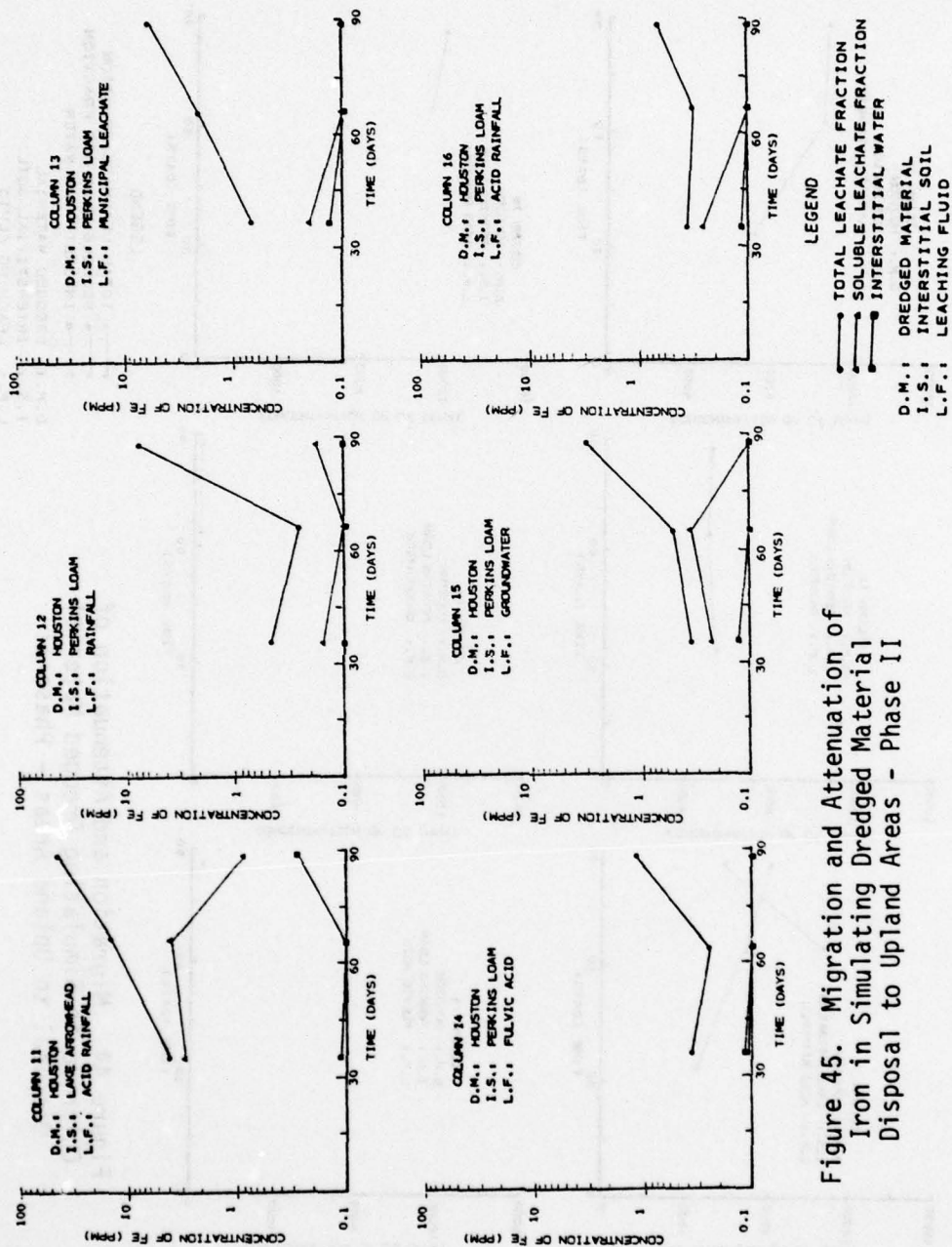


Figure 45. Migration and Attenuation of Iron in Simulating Dredged Material Disposal to Upland Areas - Phase II

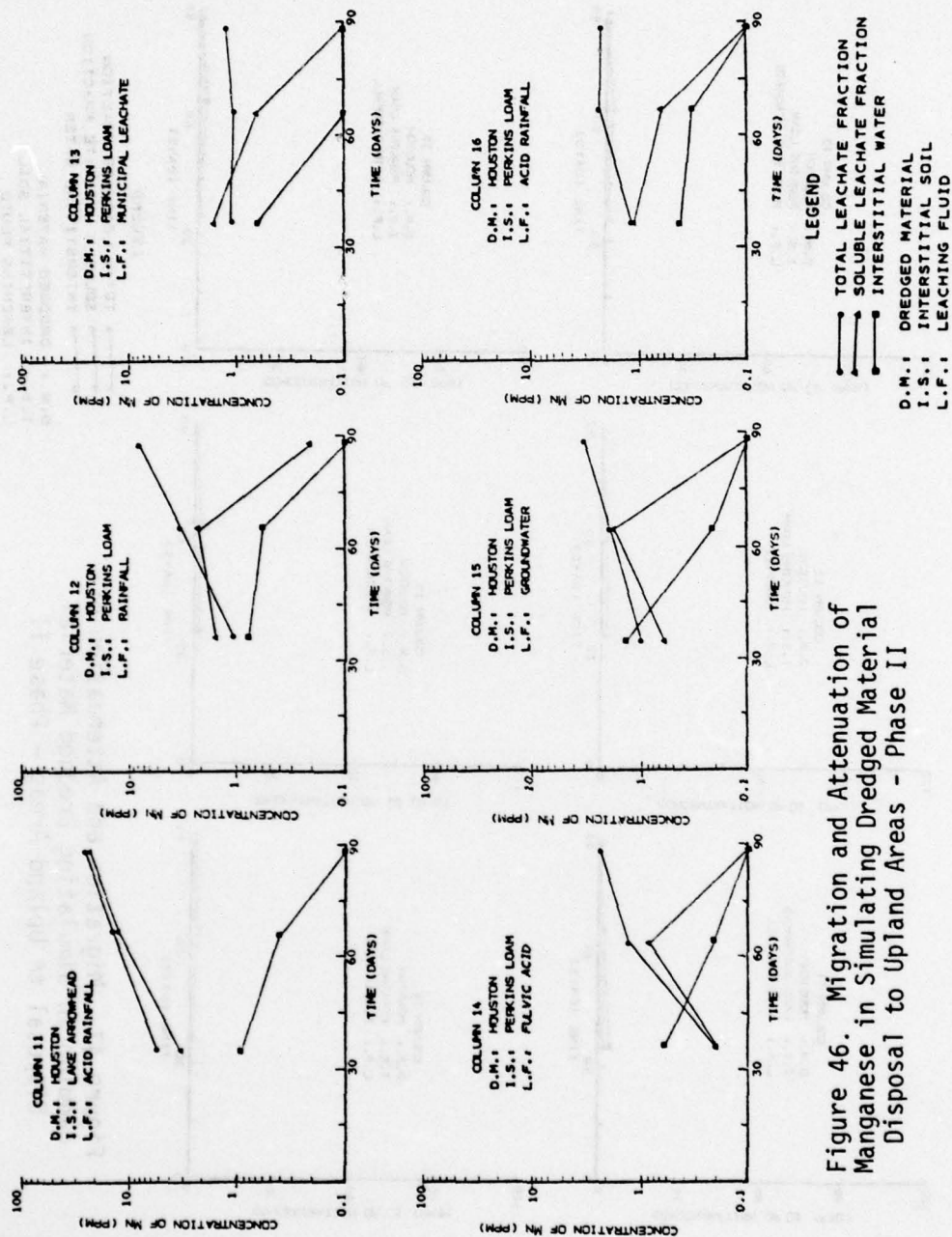


Figure 46. Migration and Attenuation of Manganese in Simulating Dredged Material Disposal to Upland Areas - Phase II

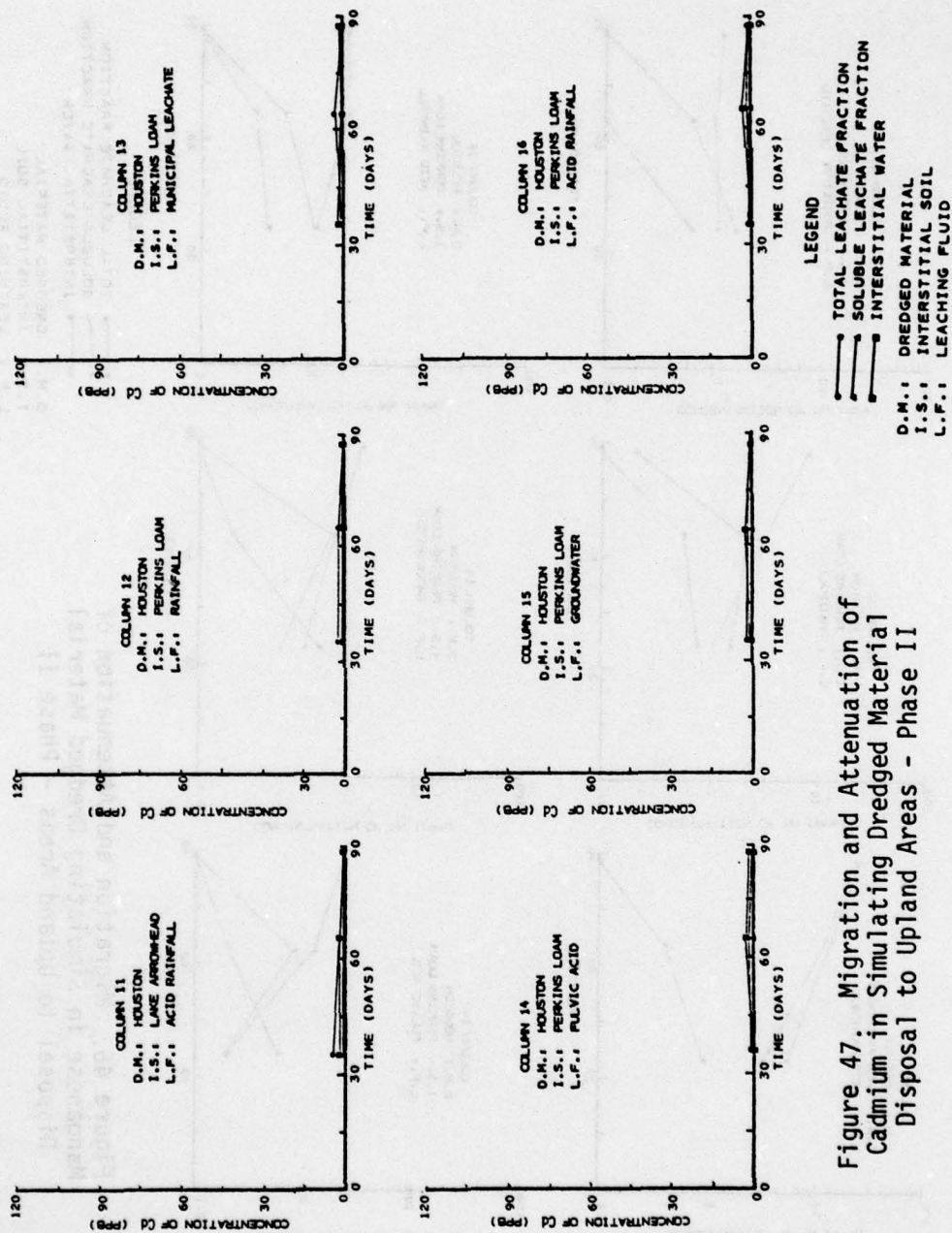


Figure 47. Migration and Attenuation of Cadmium in Simulating Dredged Material Disposal to Upland Areas - Phase II

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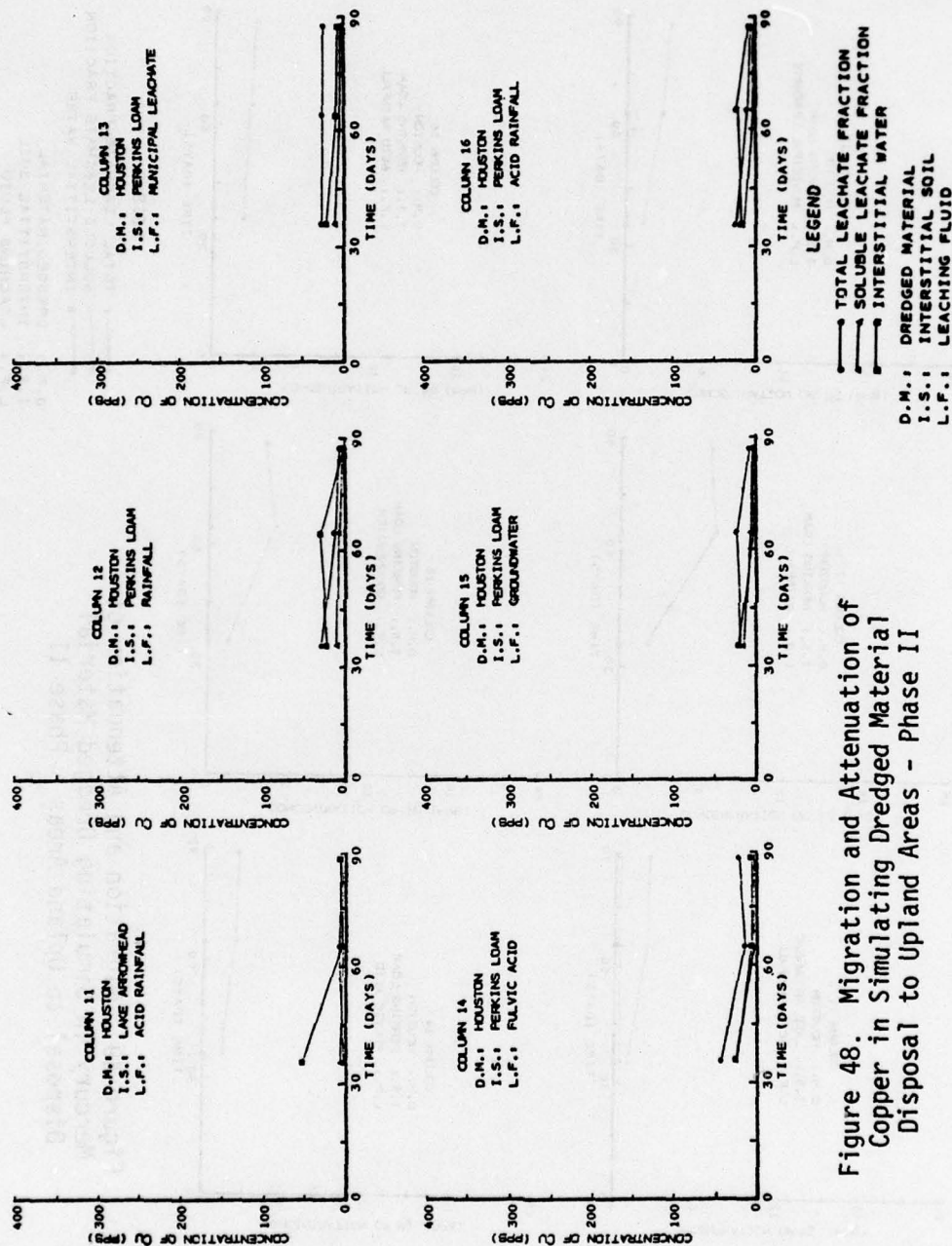


Figure 48. Migration and Attenuation of Copper in Simulating Dredged Material Disposal to Upland Areas - Phase II

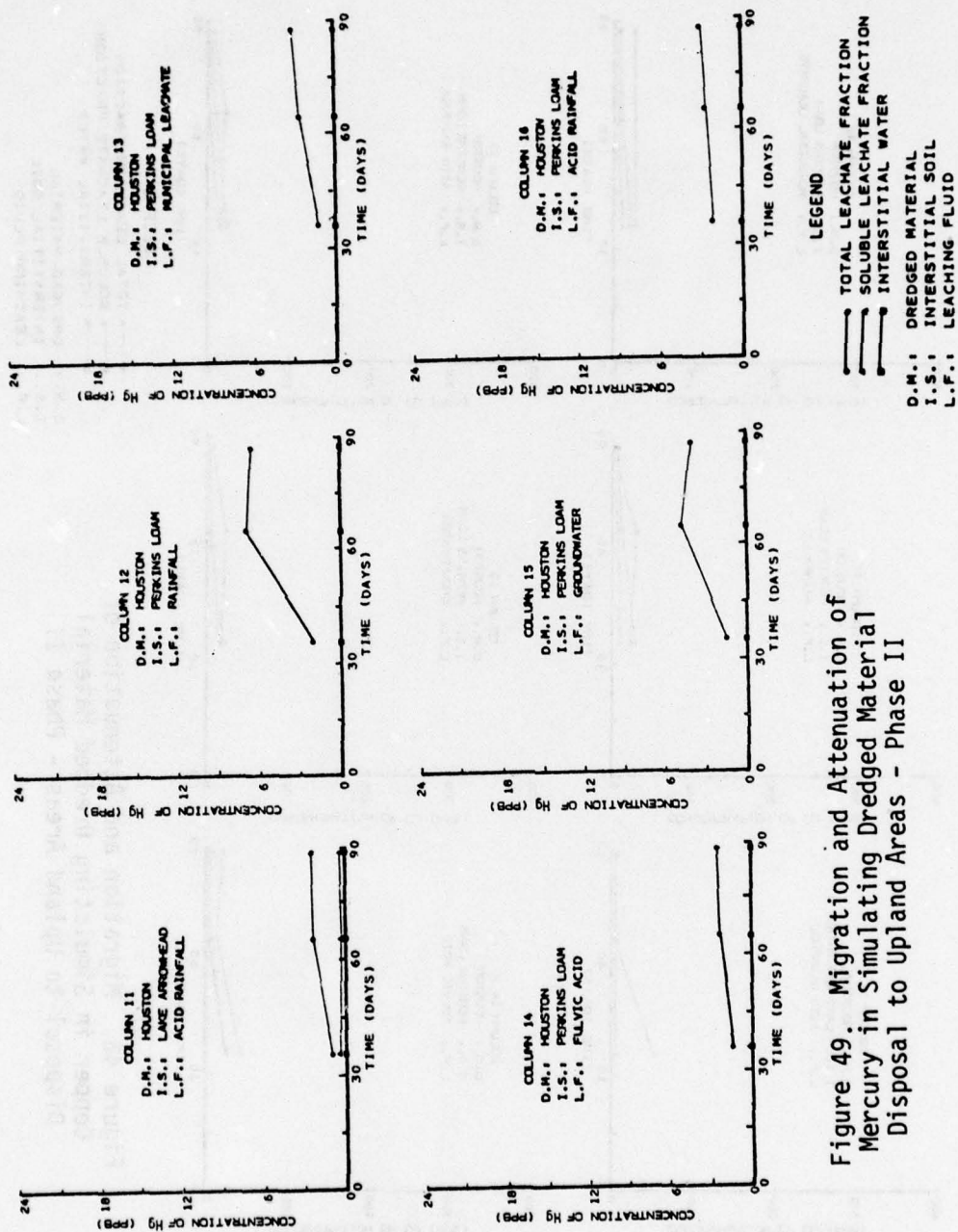


Figure 49. Migration and Attenuation of Mercury in Simulating Dredged Material Disposal to Upland Areas - Phase II

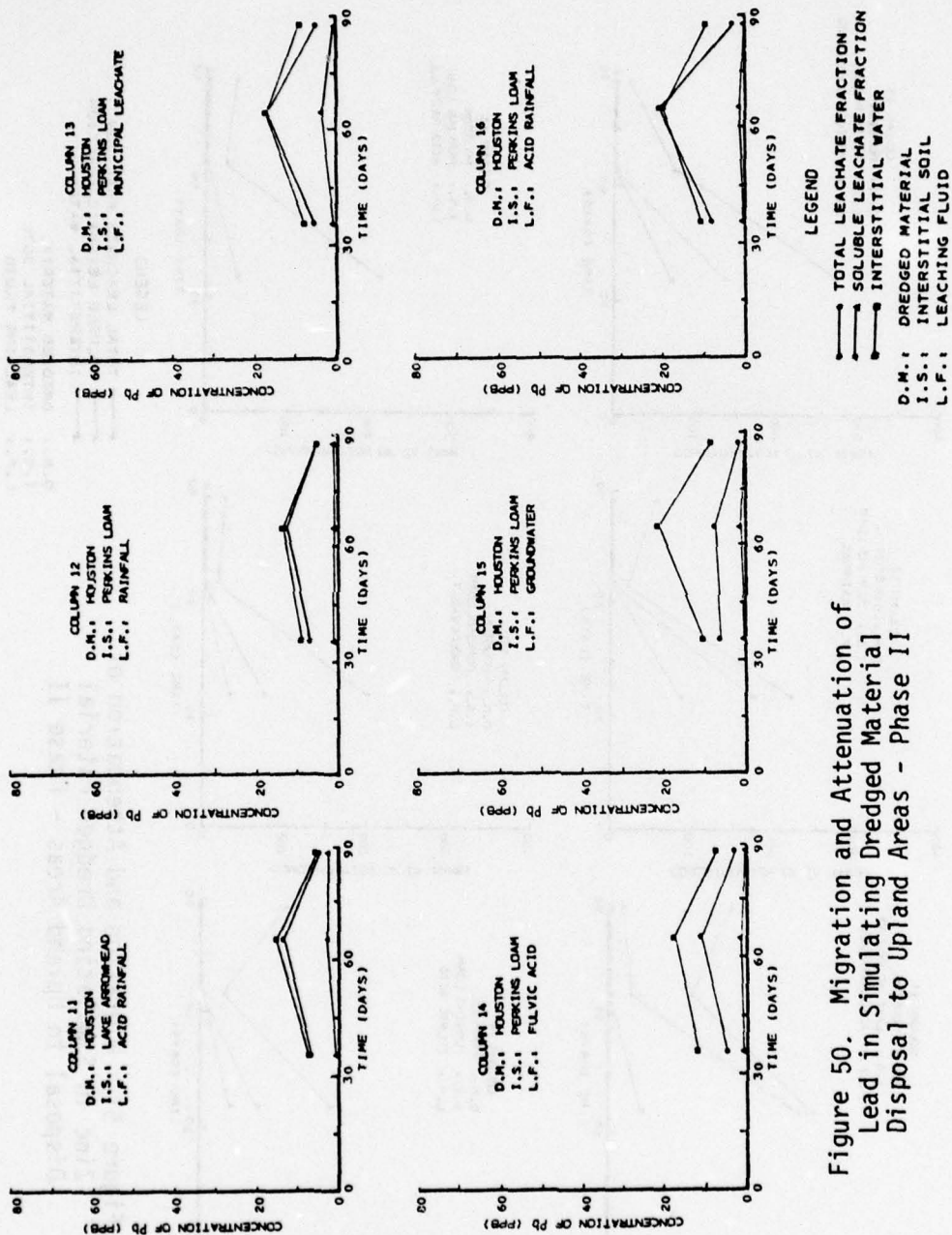


Figure 50. Migration and Attenuation of Lead in Simulating Dredged Material Disposal to Upland Areas - Phase II

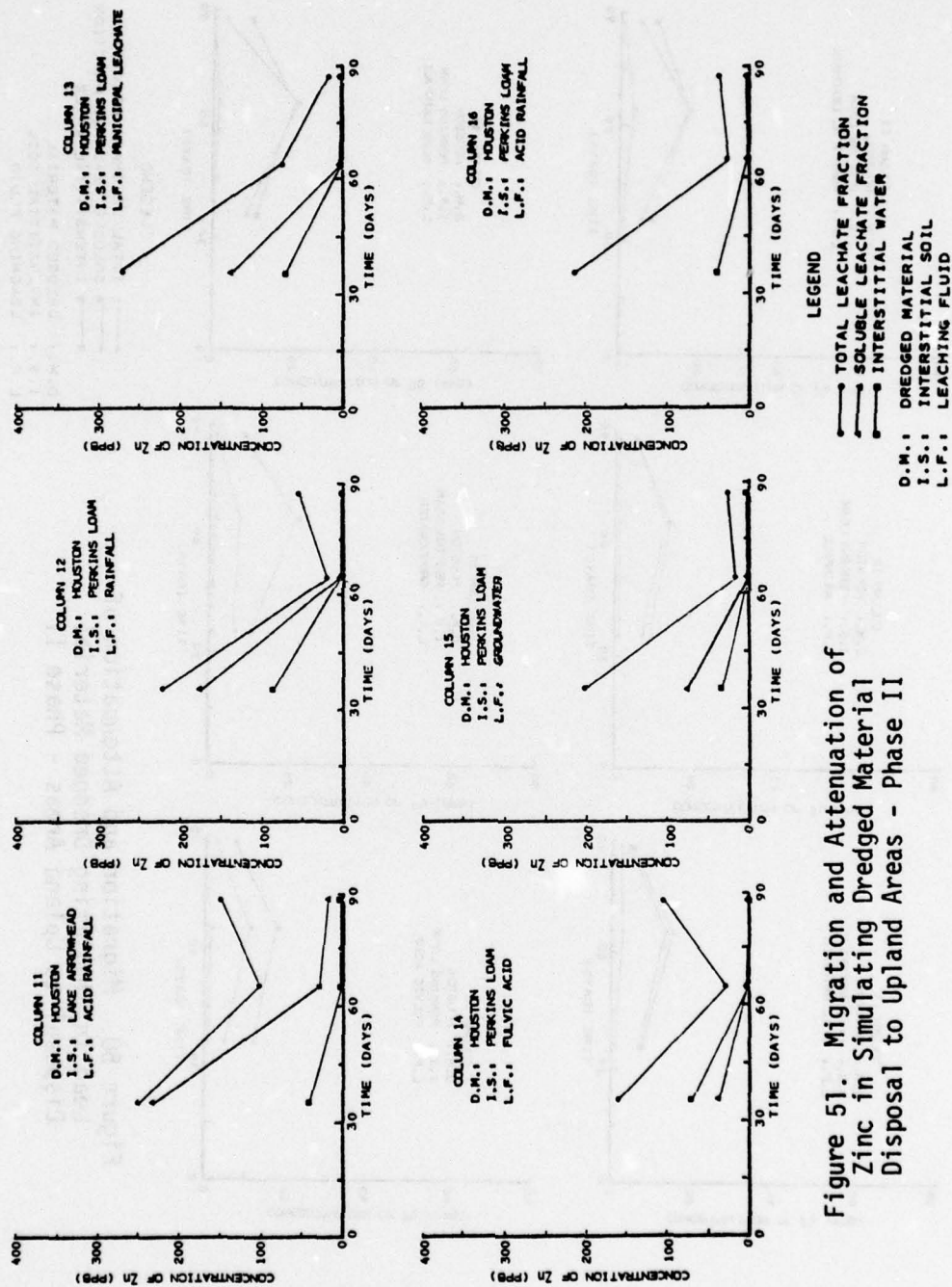


Figure 51. Migration and Attenuation of Zinc in Simulating Dredged Material Disposal to Upland Areas - Phase II

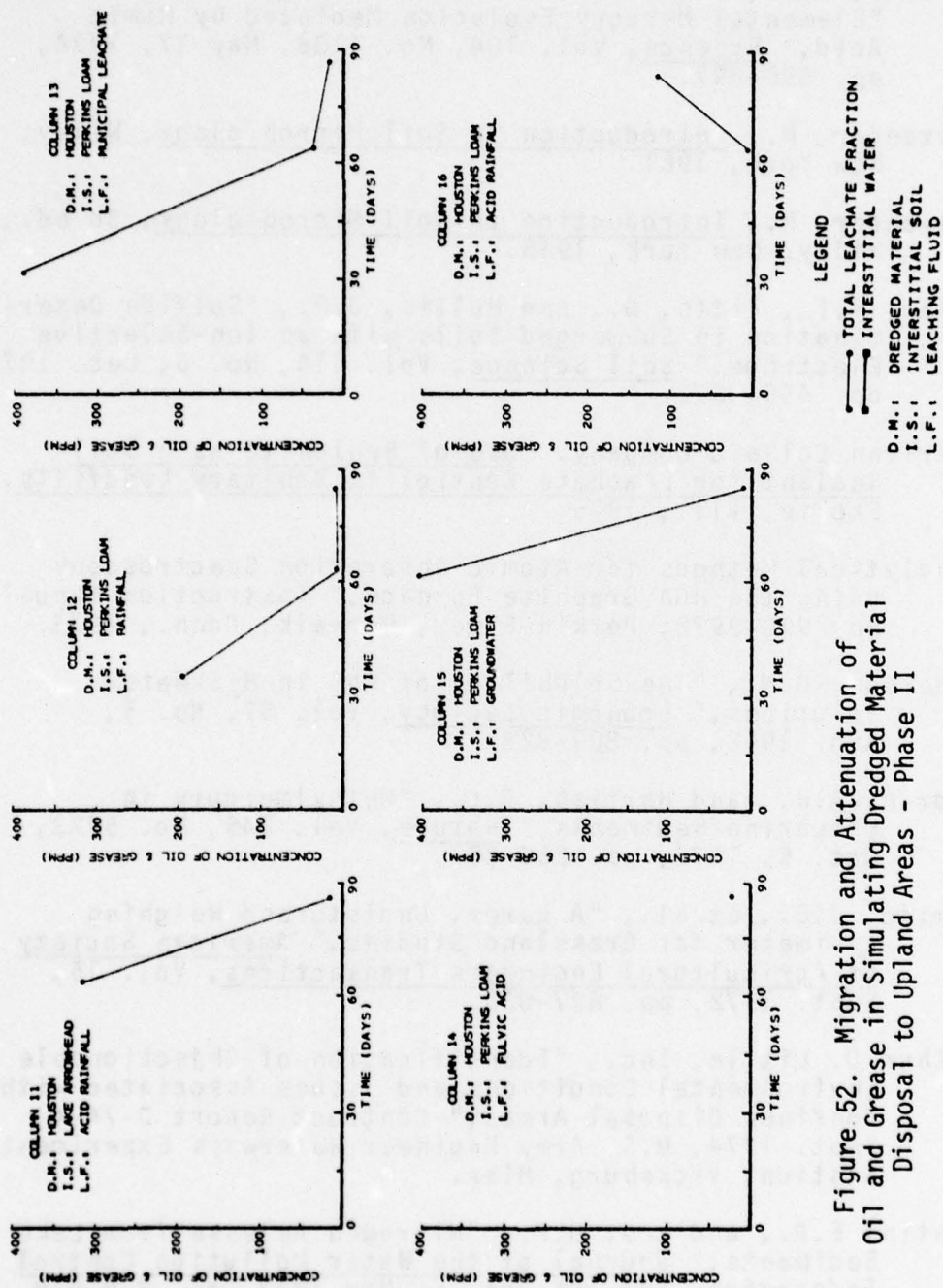


Figure 52. Migration and Attenuation of Oil and Grease in Simulating Dredged Material Disposal to Upland Areas - Phase II

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APPENDIX A :

ANALYTICAL PROCEDURES

Alkalinity

Determination of alkalinity was performed by the phenolphthalein indicator method. The sample was acidified and then back-titrated with NaOH using phenolphthalein as the indicator (Standard Methods, 14th ed., pp. 278-281).

Cation Exchange Capacity

Cation exchange capacity was determined by the sodium saturation method (Methods of Soil Analysis, pp. 892-898).

Exchangeable Cations

The soil sample was extracted with ammonium acetate. Heavy metals (Na, Ca, Mg, Hg, Pb, Cd, Cu, K, Zn, Fe, and Mn) were determined on this extract by atomic absorption.

Chloride (Cl^-)

Chloride levels were determined by utilization of the selective ion electrode method, as specified in "Ion Selective Electrodes in Seawater," T. B. Warner, Marine Technology.

Chlorinated Pesticides

Chlorinated pesticides were determined by utilizing gas chromatography with an electron capture detector, as prescribed in Standard Methods, 13th ed, pp. 100-107; Pesticide Analytical Manual, Revised September 1972; and Analysis of Pesticide Residues in Human and Environmental Samples, J. F. Thompson, ed., Revised 1972. The extraction procedures for chlorinated pesticide analysis are presented in detail in the discussions on polychlorinated biphenyl determination.

Polychlorinated Biphenyls

Polychlorinated biphenyls were determined by utilizing solvent phase partitioning and electron capture gas chromatography, with the confirmatory step being after dehydrochlorination, as described in Standard Methods, 13th ed., pp. 100-107; Analysis of Pesticide Residues in Human and Environmental Samples, J. F. Thompson, ed., Revised 1972; and Pesticide Analytical Manual, Revised September 1972.

To determine chlorinated hydrocarbon (both chlorinated pesticides and PCB's) levels in both dredged material and soil, the following extraction procedures were utilized.

Ten grams of wet dredged material/soil were weighed in a 500-ml Erlenmeyer flask with a ground glass stopper, while another 10 g of dredged material/soil were weighed to determine moisture content. Then 250 ml of acetonitrile (pesticide quality, Mallinkrodt) were added to the flask, which was shaken for 1 hour on a Gyrotory shaker. The sample was stored overnight at a constant temperature of $14 \pm 2^{\circ}\text{C}$. The sample was again shaken for 1 hour and filtered through 5 g of celite (celite 545, Sargent Welch) media on Whatman No. 4 filter paper under a modest vacuum. Another 100 ml of acetonitrile were added to avoid the possible loss of chlorinated hydrocarbons on the flask wall, celite, or residue. The filtrate was transferred to a 500-ml Kuderna-Danish concentrator and concentrated to 5 ml on a water bath. The concentrated extract (filtrate) was transferred to a 1,000-ml separatory funnel containing 200 ml of double-distilled water and 10 ml of saturated aqueous NaCl. Eight ml of petroleum ether (pesticide quality) were used to clean the concentrator and were also added to the separatory funnel. The

funnel was shaken by hand for 5 minutes and then kept stationary until a clear separation of phases occurred. The aqueous phase (bottom layer) was drained into another separatory funnel containing 80 ml of petroleum ether for the second extraction. The extraction was repeated twice. After the third extraction, the aqueous phase was discarded, and all petroleum ether extracts were collected into a Kuderna-Danish concentrator. After the petroleum ether extract was concentrated to approximately 5 ml, it was eluted on the prepared activated florosil column.

Because sulfur is present in large amounts in every sediment, every extract was treated with mercury to remove sulfur before injection into the gas chromatograph.

Conductivity

Conductivity was measured by using a commercially available Labline mho meter, (Standard Methods, 14th ed., pp. 71-75).

Ammonia-Nitrogen ($\text{NH}_3\text{-N}$)

The determination of ammonia nitrogen in the leachate and interstitial water was performed by the selective ion electrode method, as specified by Methods for Chemical Analysis of Water and Wastes, pp. 165-167. Ammonia nitrogen levels in dredged material/soil were determined by the Kjeldahl method as specified below.

Kjeldahl Nitrogen

In the total Kjeldahl procedure, amino nitrogen is converted to ammonium bisulphate in the presence of sulphuric acid, potassium sulphate, and mercuric sulphate catalyst. The mercury ammonium complex is decomposed by sodium thiosulfate during the digestion process. The ammonia is distilled from an alkaline medium and absorbed in boric acid. The ammonia

concentration is determined by titration with a standard mineral acid (Standard Methods, 14th ed., p. 437).

Nitrate-Nitrogen ($\text{NO}_3\text{-N}$)

Nitrate-nitrogen levels were analyzed by the cadmium reduction method as specified in Standard Methods, 14th ed., pp. 423-426.

Oil and Grease

Oil and grease levels were determined using the petroleum ether extraction method, as described in Standard Methods, 14th ed., p. 518.

Total Phosphorus/Orthophosphate ($\text{PO}_4\text{-P}$)

Phosphorus species were determined by the stannous chloride method, which involves the formation of molybdophosphoric acid. This acid is reduced to the intensely colored complex, molybdenum blue, by stannous chloride. (Standard Methods, 14th ed., p. 479.)

Acid digestion for the total phosphorus analysis was performed as follows. About 1 g of homogenous sample was placed in a Teflon beaker. The sample was treated with 4 to 5 drops of HF, 5 mL HNO_3 , and 3 mL HClO_4 . The mixture was digested on a hot plate until the solution almost reached dryness. The solution was cooled, and 20 mL of distilled water were added prior to centrifuging the digested sample. The supernatant was collected in a 250-mL Teflon beaker, after which the pH was adjusted to 0.2-0.3 pH units with 6N HNO_3 . The solution was passed through ANG-243 cation exchange resin (manufactured by Ionac Chemical Company), with the elutriate being collected in a beaker. The flow rate was adjusted to no greater than 4 mL per minute. The liquid was passed through the cation exchange column three times and then neutralized with 6N NaOH and 6N HNO_3 to a pH of 7. The solution was diluted to exactly 200 mL. Fifty mL of this digested sample was utilized for analysis.

pH

All pH measurements were performed using an Orion Model 701 pH Meter with glass electrode in combination with a saturated reference calomel electrode. The pH meter was standardized periodically under conditions of temperature and concentration which were as close as possible to those of the sample, using various standard pH buffer solutions (pH 4, 7, and 10) (Standard Methods, 14th ed., pp. 460-461).

Total Organic Carbon (TOC)

Total organic carbon was determined using a Beckman 915 Carbonaceous Analyzer, as specified in Methods for Chemical Analysis of Water and Wastes, pp. 236-240.

Total Sulfides (ΣS^{2-})

The determination of sulfides was performed by the titrimetric iodine method, as described in the 14th edition of Standard Methods, (p. 505).

Cadmium, Calcium, Copper, Iron, Lead, Magnesium, Manganese Mercury, Potassium, Sodium, Zinc

Because all of the heavy metals under consideration could readily form complex ions with organic constituents in the leachate, the organic matter was generally digested in a presample preparation step. Either a mixture of nitric and sulfuric acids was used, or chloric acids were employed under conditions of extremely difficult refractory organic matter.

Sample preparation was accomplished prior to atomic absorption spectroscopy determination of the heavy metals cadmium, calcium, copper, iron, lead, magnesium, manganese, mercury, potassium, sodium, and zinc in sediment and soil samples as follows:

1. Digestion (except Hg) - A measured volume of leachate or about 1 g of wet sediment, whose moisture content had already been determined, was placed into a Teflon beaker. The sample was digested with 6 ml of nitric acid, 4 ml of hydrofluoric acid, and 3 ml of perchloric acid, in a covered Teflon beaker at approximately 175°C until the particulates disappeared. After evaporation to about 2 ml, the sample was diluted to a fixed volume and centrifuged, if necessary, to eliminate undigested particulates.
2. Digestion for mercury - A 5-g measured volume of leachate or of well-mixed sample were treated with 20 ml Ultrex HNO₃ and 15 ml KNO₃ in an Erlenmeyer flask. The flask was sealed and heated in a 70°C constant temperature water bath for 12 hours. The digested sample in the flask was allowed to cool and then centrifuged. The supernatant was collected in a 100-ml volumetric flask, and 1:1 HNO₃ solution was added to the mark.

The aforementioned trace metals were determined by the following methods:

| <u>Element</u> | <u>Method</u> |
|----------------|-----------------------------|
| Cadmium | Heated graphite atomization |
| Calcium | Flame atomic absorption |
| Copper | Heated graphite atomization |
| Iron | Heated graphite atomization |
| Lead | Heated graphite atomization |
| Magnesium | Flame atomic absorption |
| Manganese | Heated graphite atomization |
| Mercury | Cold vapor |
| Potassium | Emission spectroscopy |
| Sodium | Emission spectroscopy |
| Zinc | Heated graphite atomization |

Individual analyses were performed according to the specified operating conditions provided in the equipment manufacturer's analytical methods manual.

Grain-Size Distribution

Grain-size distribution was determined by both the sieving and hydrometer methods as described in Methods of Soil Analysis, pp. 457-567.

Interstitial Water Volume

Interstitial water volume was determined by the Carter Press squeeze method.

Permeability

Permeability was determined by the permeameter method as specified in Methods of Soil Analysis, pp. 248-252.

Density

Density was determined by the core method as specified in Methods of Soil Analysis, pp. 378-380.

Moisture Content

Moisture content was determined by placing the sample in an evaporation dish and drying at 103 to 105°C (Standard Methods, 14th ed., p. 91).

In accordance with letter from DAEN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

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A study of leachate from dredged material in upland areas and/or in productive uses / by James L. Mang ... [et al.], SCS Engineers, Long Beach, California. Vicksburg, Miss. : U. S. Waterways Experiment Station ; Springfield, Va. : available from National Technical Information Service, 1978. 428, 7 p. : ill. ; 27 cm. (Technical report - U. S. Army Engineer Waterways Experiment Station ; D-78-20)

Prepared for Office, Chief of Engineers, U. S. Army, Washington, D. C., under Contract No. DACW39-76-C-0069 (DMRP Work Unit No. 2D02)

References: p. 208-224.

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TA7.W34 no.D-78-20